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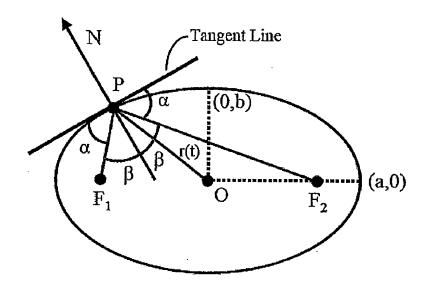
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[Continued on next page]

(54) Title: SYSTEM AND METHOD OF COMPUTING AND RENDERING THE NATURE OF POLYATOMIC MOLECULES AND POLYATOMIC MOLECULAR IONS



(57) Abstract: A method and system of physically solving the charge, mass, and current density functions of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species using Maxwell's equations and computing and rendering the physical nature of the chemical bond using the solutions. The results can be displayed on visual or graphical media. The display can be static or dynamic such that electron motion and specie's vibrational, rotational, and translational motion can be displayed in an embodiment. The displayed information is useful to anticipate reactivity and physical properties. The insight into the nature of the chemical bond of at least one specie can permit the solution and display of those of other species to provide utility to anticipate their reactivity and physical properties.

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# SYSTEM AND METHOD OF COMPUTING AND RENDERING THE NATURE OF POLYATOMIC MOLECULES AND POLYATOMIC MOLECULAR IONS

This application claims priority to U.S. Application Nos.: 60/730,882, filed October 28, 2005; 60/732,154, filed November 2, 2005; 60/737,744, filed November 18, 2005; 60/758,528, filed January 13, 2006; 60/780,518, filed March 9, 2006; 60/788,694, filed April 4, 2006; 60/812,590, filed June 12, 2006; and 60/815,253, June 21, 2006, the complete disclosures of which are incorporated herein by reference.

#### 10 Field of the Invention:

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This invention relates to a system and method of physically solving the charge, mass, and current density functions of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species, and computing and rendering the nature of these species using the solutions. The results can be displayed on visual or graphical media. The displayed information provides insight into the nature of these species and is useful to anticipate their reactivity, physical properties, and spectral absorption and emission, and permits the solution and display of other species.

Rather than using postulated unverifiable theories that treat atomic particles as if they were not real, physical laws are now applied to atoms and ions. In an attempt to provide some physical insight into atomic problems and starting with the same essential physics as Bohr of the  $e^-$  moving in the Coulombic field of the proton with a true wave equation, as opposed to the diffusion equation of Schrödinger, a classical approach is explored which yields a model that is remarkably accurate and provides insight into physics on the atomic level. The proverbial view deeply seated in the wave-particle duality notion that there is no large-scale physical counterpart to the nature of the electron is shown not to be correct. Physical laws and intuition may be restored when dealing with the wave equation and quantum atomic problems.

Specifically, a theory of classical quantum mechanics (CQM) was derived from first principles as reported previously [reference Nos. 1-8] that successfully applies physical laws to the solution of atomic problems that has its basis in a breakthrough in the understanding of the stability of the bound electron to radiation. Rather than using the postulated Schrödinger boundary condition: " $\Psi \to 0$  as  $r \to \infty$ ", which leads to a purely mathematical model of the electron, the constraint is based on experimental observation. Using Maxwell's equations, the

classical wave equation is solved with the constraint that the bound n = 1-state electron cannot radiate energy. Although it is well known that an accelerated point particle radiates, an extended distribution modeled as a superposition of accelerating charges does not have to radiate. A simple invariant physical model arises naturally wherein the predicted results are extremely straightforward and internally consistent requiring minimal math, as in the case of the most famous equations of Newton, Maxwell, Einstein, de Broglie, and Planck on which the model is based. No new physics is needed; only the known physical laws based on direct observation are used.

Applicant's previously filed WO2005/067678 discloses a method and system of physically solving the charge, mass, and current density functions of atoms and atomic ions and computing and rendering the nature of these species using the solutions. The complete disclosure of this published PCT application is incorporated herein by reference.

Applicant's previously filed WO2005/116630 discloses a method and system of physically solving the charge, mass, and current density functions of excited states of atoms and atomic ions and computing and rendering the nature of these species using the solutions. The complete disclosure of this published PCT application is incorporated herein by reference.

Applicant's previously filed U.S. Published Patent Application No. 20050209788A1, relates to a method and system of physically solving the charge, mass, and current density functions of hydrogen-type molecules and molecular ions and computing and rendering the nature of the chemical bond using the solutions. The complete disclosure of this published application is incorporated herein by reference.

#### Background of the Invention

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The old view that the electron is a zero or one-dimensional point in an all-space probability wave function  $\Psi(x)$  is not taken for granted. The theory of classical quantum mechanics (CQM), derived from first principles, must successfully and consistently apply physical laws on all scales [1-8]. Stability to radiation was ignored by all past atomic models. Historically, the point at which QM broke with classical laws can be traced to the issue of nonradiation of the one electron atom. Bohr just postulated orbits stable to radiation with the further postulate that the bound electron of the hydrogen atom does not obey Maxwell's equations—rather it obeys different physics [1-12]. Later physics was replaced by "pure mathematics" based on the notion of the inexplicable wave-particle duality nature of electrons

which lead to the Schrödinger equation wherein the consequences of radiation predicted by Maxwell's equations were ignored. Ironically, Bohr, Schrödinger, and Dirac used the Coulomb potential, and Dirac used the vector potential of Maxwell's equations. But, all ignored electrodynamics and the corresponding radiative consequences. Dirac originally attempted to solve the bound electron physically with stability with respect to radiation according to Maxwell's equations with the further constraints that it was relativistically invariant and gave rise to electron spin [13]. He and many founders of QM such as Sommerfeld, Bohm, and Weinstein wrongly pursued a planetary model, were unsuccessful, and resorted to the current mathematical-probability-wave model that has many problems [9-16]. Consequently, Feynman for example, attempted to use first principles including Maxwell's equations to discover new physics to replace quantum mechanics [17].

Physical laws may indeed be the root of the observations thought to be "purely quantum mechanical", and it was a mistake to make the assumption that Maxwell's electrodynamic equations must be rejected at the atomic level. Thus, in the present approach, the classical wave equation is solved with the constraint that a bound n = 1-state electron cannot radiate energy.

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Herein, derivations consider the electrodynamic effects of moving charges as well as the Coulomb potential, and the search is for a solution representative of the electron wherein there is acceleration of charge motion without radiation. The mathematical formulation for zero radiation based on Maxwell's equations follows from a derivation by Haus [18]. The function that describes the motion of the electron must not possess spacetime Fourier components that are synchronous with waves traveling at the speed of light. Similarly, nonradiation is demonstrated based on the electron's electromagnetic fields and the Poynting power vector.

It was shown previously [1-8] that CQM gives closed form solutions for the atom including the stability of the n=1 state and the instability of the excited states, the equation of the photon and electron in excited states, and the equation of the free electron and photon, which predict the wave particle duality behavior of particles and light. The current and charge density functions of the electron may be directly physically interpreted. For example, spin angular momentum results from the motion of negatively charged mass moving systematically, and the equation for angular momentum,  $\mathbf{r} \times \mathbf{p}$ , can be applied directly to the wave function (a current density function) that describes the electron. The magnetic moment of a Bohr magneton, Stern Gerlach experiment, g factor, Lamb shift, resonant line width and

shape, selection rules, correspondence principle, wave particle duality, excited states, reduced mass, rotational energies, and momenta, orbital and spin splitting, spin-orbital coupling, Knight shift, and spin-nuclear coupling, and elastic electron scattering from helium atoms, are derived in closed-form equations based on Maxwell's equations. The calculations agree with experimental observations.

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The Schrödinger equation gives a vague and fluid model of the electron. Schrödinger interpreted  $e\Psi^*(x)\Psi(x)$  as the charge-density or the amount of charge between x and x+dx ( $\Psi^*$  is the complex conjugate of  $\Psi$ ). Presumably, then, he pictured the electron to be spread over large regions of space. After Schrödinger's interpretation, Max Born, who was working with scattering theory, found that this interpretation led to inconsistencies, and he replaced the Schrödinger interpretation with the probability of finding the electron between x and x+dx as

$$\int \Psi(x)\Psi^*(x)dx \tag{1}$$

Born's interpretation is generally accepted. Nonetheless, interpretation of the wave function is a never-ending source of confusion and conflict. Many scientists have solved this problem by conveniently adopting the Schrödinger interpretation for some problems and the Born interpretation for others. This duality allows the electron to be everywhere at one time—yet have no volume. Alternatively, the electron can be viewed as a discrete particle that moves here and there (from r = 0 to  $r = \infty$ ), and  $\Psi\Psi$ \* gives the time average of this motion.

In contrast to the failure of the Bohr theory and the nonphysical, adjustable-parameter approach of quantum mechanics, multielectron atoms [1, 4] and the nature of the chemical bond [1, 5] are given by exact closed-form solutions containing fundamental constants only. Using the nonradiative wave equation solutions that describe the bound electron having conserved momentum and energy, the radii are determined from the force balance of the electric, magnetic, and centrifugal forces that corresponds to the minimum of energy of the system. The ionization energies are then given by the electric and magnetic energies at these radii. The spreadsheets to calculate the energies from exact solutions of one through twenty-electron atoms are given in '06 Mills GUT [1] and are available from the internet [19]. For 400 atoms and ions, as well as hundreds of molecules, the agreement between the predicted and experimental results is remarkable.

The background theory of classical quantum mechanics (CQM) for the physical solutions of atoms and atomic ions is disclosed in R. Mills, The Grand Unified Theory of

Classical Quantum Mechanics, January 2000 Edition, BlackLight Power, Inc., Cranbury, New Jersey, (" '00 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512; R. Mills, The Grand Unified Theory of Classical Quantum Mechanics, September 2001 Edition, BlackLight Power, Inc., Cranbury, New Jersey, Distributed by

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- BlackLight Power, Inc., Cranbury, New Jersey, (" '05 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512 (posted at <a href="www.blacklightpower.com">www.blacklightpower.com</a>); R. L. Mills, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number
- 2005936834, (" '06 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512 (posted at <a href="http://www.blacklightpower.com/bookdownload.shtml">http://www.blacklightpower.com/bookdownload.shtml</a>); in prior PCT applications PCT/US02/35872; PCT/US02/06945; PCT/US02/06955; PCT/US01/09055; PCT/US01/25954; PCT/US00/20820; PCT/US00/20819; PCT/US00/09055; PCT/US99/17171;
- PCT/US99/17129; PCT/US 98/22822; PCT/US98/14029; PCT/US96/07949; PCT/US94/02219; PCT/US91/08496; PCT/US90/01998; and PCT/US89/05037 and U.S. Patent No. 6,024,935; the entire disclosures of which are all incorporated herein by reference (hereinafter "Mills Prior Publications").

The following list of references, which are also incorporated herein by reference in their entirety, are referred to in the above sections using [brackets]:

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  ISBN 0963517171, Library of Congress Control Number 2005936834; posted at
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209-211.

- 18. Haus, H. A., "On the radiation from point charges", American Journal of Physics, 54, (1986), pp. 1126-1129.
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#### SUMMARY OF THE INVENTION

The present invention, an exemplary embodiment of which is also referred to as Millsian software, stems from a new fundamental insight into the nature of the atom. Applicant's new theory of <u>Classical Quantum Mechanics</u> (CQM) reveals the nature of atoms and molecules using classical physical laws for the first time. As discussed above, traditional quantum mechanics can solve neither multi-electron atoms nor molecules exactly. By contrast, CQM produces exact, closed-form solutions containing physical constants only for even the most complex atoms and molecules.

The present invention is the first and only molecular modeling program ever built on the CQM framework. All the major functional groups that make up most organic molecules have been solved exactly in closed-form solutions with CQM. By using these functional groups as building blocks, or independent units, a potentially infinite number of organic molecules can be solved. As a result, the present invention can be used to visualize the exact 3D structure and calculate the heat of formation of almost any organic molecule.

For the first time, the significant building-block molecules of chemistry have been successfully solved using classical physical laws in exact closed-form equations having fundamental constants only. The major functional groups have been solved from which molecules of infinite length can be solved almost instantly with a computer program. The predictions are accurate within experimental error for over 375 exemplary molecules.

Applicant's CQM is the theory that physical laws (Maxwell's Equations, Newton's Laws, Special and General Relativity) must hold on all scales. The theory is based on an often overlooked result of Maxwell's Equations, that an extended distribution of charge may, under certain conditions, accelerate without radiating. This "condition of no radiation" is invoked to solve the physical structure of subatomic particles, atoms, and molecules.

In exact closed-form equations with physical constants only, solutions to thousands of known experimental values arise that were beyond the reach of previous outdated theories. These include the electron spin, g-factor, multi-electron atoms, excited states, polyatomic molecules, wave-particle duality and the nature of the photon, the masses and families of

fundamental particles, and the relationships between fundamental laws of the universe that reveal why the universe is accelerating as it expands. CQM is successful to over 85 orders of magnitude, from the level of quarks to the cosmos. Applicant now has over 65 peer-reviewed journal articles and also books discussing the CQM and supporting experimental evidence.

The molecular modeling market was estimated to be a two-billion-dollar per year industry in 2002, with hundreds of millions of government and industry dollars invested in computer algorithms and supercomputer centers. This makes it the largest effort of computational chemistry and physics.

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The present invention's advantages over other models includes: Rendering true molecular structures; Providing precisely all characteristics, spatial and temporal charge distributions and energies of every electron in every bond, and of every bonding atom; Facilitating the identification of biologically active sites in drugs; and Facilitating drug design.

An objective of the present invention is to solve the charge (mass) and current-density functions of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species from first principles. In an embodiment, the solution for the polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species is derived from Maxwell's equations invoking the constraint that the bound electron before excitation does not radiate even though it undergoes acceleration.

Another objective of the present invention is to generate a readout, display, or image of the solutions so that the nature of polyatomic molecules, polyatomic molecular ions, diatomic molecular, molecular radicals, molecular ions, or any portion of these species be better understood and potentially applied to predict reactivity and physical and optical properties.

Another objective of the present invention is to apply the methods and systems of solving the nature of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species and their rendering to numerical or graphical form to all atoms and atomic ions.

These objectives and other objectives are obtained by a system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising

physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.

Also provided is a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

The presented exact physical solutions for known species of the group of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any functional group therein, can be applied to other species. These solutions can be used to predict the properties of other species and engineer compositions of matter in a manner which is not possible using past quantum mechanical techniques. The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. Not only can new stable compositions of matter be predicted, but now the structures of combinatorial chemistry reactions can be predicted.

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Pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the specie to be identified from the common spatial charge-density functions of a series of active species. Novel drugs can now be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the drug.

The system can be used to calculate conformations, folding, and physical properties, and the exact solutions of the charge distributions in any given specie are used to calculate the fields. From the fields, the interactions between groups of the same specie or between groups on different species are calculated wherein the interactions are distance and relative orientation dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

Embodiments of the system for performing computing and rendering of the nature of the polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species using the physical solutions may comprise a general purpose computer. Such a general purpose computer may have any number of basic configurations. For example, such a general purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input means, such as a keyboard or mouse, a display device, and a printer or other output device. A system implementing the present invention can also comprise a special purpose computer or other hardware system and all should be included within its scope.

Although not preferred, any of the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

#### BRIEF DESCRIPTION OF THE DRAWINGS

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- Fig. 1 illustrates an elliptical current element of the prolate spheroidal MO;
- Fig. 2 illustrates the ellipsoidal current-density surface obtained by stretching  $Y_0^0(\theta, \phi)$  along the semimajor axis;
- Fig. 3 illustrates the angular momentum components of the MO and S;
- 20 Fig. 4 illustrates cross section of an atomic orbital;
  - Fig. 5 illustrates A. Prolate spheroid MO;
  - Fig. 6 illustrates the equilateral triangular  $H_3^+(1/p)$ ;
  - Fig. 7 illustrates the cross section of the OH MO;
  - Fig. 8 illustrates OH MO comprising the superposition of the  $H_2$ -type ellipsoidal MO and the  $O2p_y$  AO with a relative charge-density of 0.75 to 1.25;
  - Fig. 9 illustrates  $H_2O$  MO comprising the linear combination of two O-H -bond MOs;
  - Fig. 10 illustrates the cross section of the NH MO showing the axes, angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $N2p_x$  AO;
  - Fig. 11 illustrates NH MO comprising the superposition of the  $H_2$ -type ellipsoidal MO and the  $N2p_x$  AO with a relative charge-density of 0.75 to 1.25;
  - Fig. 12 illustrates  $NH_2$  MO comprising the linear combination of two N-H-bond MOs;

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- Fig. 13 illustrates  $NH_3$  MO comprising the linear combination of three N-H-bonds;
- Fig. 14 illustrates the cross section of the CH MO showing the axes, angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  HO;
- Fig. 15 illustrates CH MO comprising the superposition of the  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO with a relative charge-density of 0.75 to 1.25; 5
  - Fig. 16 illustrates  $CH_2$  MO comprising the linear combination of two C-H-bond MOs;
  - Fig. 17 illustrates  $CH_3$  MO comprising the linear combination of three C-H-bond MOs;
  - Fig. 18 illustrates  $CH_4$  MO comprising the linear combination of four C-H-bond MOs formed by the superposition of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO;
- Fig. 19 illustrates the cross section of the  $N_2$  MO;
  - Fig. 20 illustrates  $N_2$  MO comprising the  $\sigma$  MO ( $H_2$ -type MO) with N atoms at the foci;
  - Fig. 21 illustrates the cross section of the  $O_2$  MO;
  - Fig. 22 illustrates  $O_2$  MO comprising the  $\sigma$  MO ( $H_2$ -type MO);
  - Fig. 23 illustrates the cross section of the  $F_2$  MO;
- Fig. 24 illustrates  $F_2$  MO comprising the  $\sigma$  MO ( $H_2$ -type MO) with F atoms at the foci;
  - Fig. 25 illustrates the cross section of the  $Cl_2$  MO;
  - Fig. 26 illustrates  $Cl_2$  MO comprising the superposition of the  $H_2$ -type ellipsoidal MO and the two Cl3sp<sup>3</sup> HOs,
  - Fig. 27 illustrates the cross section of the CN MO;
- Fig. 28 illustrates CN MO; 20
  - Fig. 29 illustrates the cross section of the CO MO;
  - Fig. 30 illustrates CO MO;
  - Fig. 31 illustrates the cross section of the NO MO;
  - Fig. 32 illustrates NO MO;
- Fig. 33 illustrates the cross section of the  $CO_2$  MO;
  - Fig. 34 illustrates CO<sub>2</sub> MO;
  - Fig. 35 illustrates the cross section of the NO<sub>2</sub> MO;
  - Fig. 36 illustrates NO<sub>2</sub> MO;
  - Fig. 37 illustrates the cross section of the C-C-bond MO ( $\sigma$  MO) and one C-H-bond

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MO of ethane;

- Fig. 38 illustrates the cross section of one C-H-bond MO of ethane showing the axes, angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{ethane} 2sp^3$  HO;
- Fig. 39 illustrates  $CH_3CH_3$  MO comprising the linear combination of two sets of three C-H-bond MOs and a C-C-bond MO;
  - Fig. 40 illustrates the cross section of the C = C-bond MO ( $\sigma$  MO) and one C H-bond MO of ethylene showing the axes, angles, and point of intersection of each  $H_2$ -type ellipsoidal MO with the corresponding  $C_{ethylene} 2sp^3$  HO;
- Fig. 41 illustrates the cross section of one C-H-bond MO of ethylene showing the axes, angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{ethylene} 2sp^3$  HO;
  - Fig. 42 illustrates  $CH_2CH_2$  MO comprising the linear combination of two sets of two C-H-bond MOs and a C=C-bond MO;
- Fig. 43 illustrates the cross section of the  $C \equiv C$ -bond MO ( $\sigma$  MO) and one C-H-bond MO of acetylene showing the axes, angles, and point of intersection of each  $H_2$ -type ellipsoidal MO with the corresponding  $C_{acetylene} 2sp^3$  HO;
  - Fig. 44 illustrates CHCH MO comprising the linear combination of two C-H-bond MOs and a  $C \equiv C$ -bond MO;
- Fig. 45 illustrates the cross section of one C = C -bond MO ( $\sigma$  MO) and one C H -bond MO of benzene showing the axes, angles, and point of intersection of each  $H_2$ -type ellipsoidal MO with the corresponding  $C_{benzene} 2sp^3$  HO;
  - Fig. 46 illustrates the cross section of one C-H-bond MO of benzene showing the axes, angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{benzene} 2sp^3$  HO;
  - Fig. 47 illustrates  $C_6H_6$  MO comprising the linear combination of six sets of C-H-bond MOs bridged by C=C-bond MOs;
  - Fig. 48 illustrates the cross section of one C-C-bond MO ( $\sigma$  MO) and one C-H-bond MO of  $C_nH_{2n+2}$  showing the axes, angles, and point of intersection of each  $H_2$ -type ellipsoidal MO with the corresponding  $C_{alkane}2sp^3$  HO;

- Fig. 49 illustrates the cross section of one C-H-bond MO of  $C_nH_{2n+2}$  showing the axes, angles, and point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{alkane}2sp^3$  HO;
- Fig. 50 illustrates  $C_3H_8$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl groups and one methylene group;
- Fig. 51 illustrates  $C_4H_{10}$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl and two methylene groups;
- Fig. 52 illustrates  $C_5H_{12}$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl and three methylene groups;
- Fig. 53 illustrates  $C_6H_{14}$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl and four methylene groups;
  - Fig. 54 illustrates  $C_7H_{16}$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl and five methylene groups;
  - Fig. 55 illustrates  $C_8H_{18}$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl and six methylene groups;
  - Fig. 56 illustrates  $C_9H_{20}$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl and seven methylene groups. (A) Opaque view of the charge-density of the C-C-bond and C-H-bond MOs;
  - Fig. 57 illustrates  $C_{10}H_{22}$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl and eight methylene groups;
  - Fig. 58 illustrates  $C_{11}H_{24}$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl and nine methylene groups;
  - Fig. 59 illustrates  $C_{12}H_{26}$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl and ten methylene groups;
- 25 Fig. 60 illustrates  $C_{18}H_{38}$  MO comprising a linear combination of C-H-bond MOs and C-C-bond MOs of the two methyl and sixteen methylene groups;
  - Fig. 61.A illustrates 1,3 Butadiene;

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- Fig. 61.B illustrates 1,3 Pentadiene;
- Fig. 61.C illustrates 1,4 Pentadiene;
- 30 Fig. 61.D illustrates 1,3 Cyclopentadiene;

- Fig. 61E illustrates Cyclopentene;
- Fig. 62 illustrates Naphthalene;
- Fig. 63 illustrates Toluene;
- Fig. 64 illustrates Benzoic acid;
- 5 Fig. 65 illustrates Pyrrole;
  - Fig. 66 illustrates Furan;
  - Fig. 67 illustrates Thiophene;
  - Fig. 68 illustrates Imidazole;
  - Fig. 69 illustrates Pyridine;
- 10 Fig. 70 illustrates Pyrimidine;
  - Fig. 71 illustrates Pyrazine;
  - Fig. 72 illustrates Quinoline;
  - Fig. 73 illustrates Isoquinoline;
  - Fig. 74 illustrates Indole;
- 15 Fig. 75 illustrates Adenine;
  - Fig. 76 illustrates a block diagram of an exemplary software program; and
  - Figs. 77 and 78 illustrate pictures of an exemplary software program.

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## **Section I**

# THE NATURE OF THE CHEMICAL BOND OF HYDROGEN-TYPE MOLECULES AND MOLECULAR IONS

5

With regard to the Hydrino Theory—BlackLight Process section, the possibility of states with n=1/p is also predicted in the case of hydrogen molecular species wherein H(1/p) reacts a proton or two H(1/p) atoms react to form  $H_2^+(1/p)$  and  $H_2(1/p)$ , respectively. The natural molecular-hydrogen coordinate system based on symmetry is ellipsoidal coordinates.

- 10 The magnitude of the central field in the derivations of molecular hydrogen species is taken as the general parameter p wherein p may be an integer which may be predictive of new possibilities. Thus, p replaces the effective nuclear charge of quantum mechanics and corresponds to the physical field of a resonant photon superimposed with the field of the proton. The case with p=1 is evaluated and compared with the experimental results for
- 15 hydrogen species in Table 11.1, and the consequences that p = integer are considered in the Nuclear Magnetic Resonance Shift section.

Two hydrogen atoms react to form a diatomic molecule, the hydrogen molecule.

$$2H[a_H] \to H_2 \Big[ 2c' = \sqrt{2}a_o \Big] \tag{11.1}$$

where 2c' is the internuclear distance. Also, two hydrino atoms react to form a diatomic 20 molecule, a dihydrino molecule.

$$2H\left[\frac{a_H}{p}\right] \to H_2\left[2c' = \frac{\sqrt{2}a_o}{p}\right] \tag{11.2}$$

where p is an integer.

Hydrogen molecules form hydrogen molecular ions when they are singly ionized.

$$H_2[2c' = \sqrt{2}a_o] \to H_2[2c' = 2a_o]^+ + e^-$$
 (11.3)

25 Also, dihydrino molecules form dihydrino molecular ions when they are singly ionized.

$$H_2 \left[ 2c' = \frac{\sqrt{2}a_o}{p} \right] \rightarrow H_2 \left[ 2c' = \frac{2a_o}{p} \right]^+ + e - \tag{11.4}$$

#### HYDROGEN-TYPE MOLECULAR IONS

Each hydrogen-type molecular ion comprises two protons and an electron where the equation of motion of the electron is determined by the central field which is p times that of a proton at each focus (p is one for the hydrogen molecular ion, and p is an integer greater than one for each  $H_2^+(1/p)$ , called dihydrino molecular ion). The differential equations of motion in the case of a central field are [1]

$$m(\ddot{r} - r\dot{\theta}^2) = f(r) \tag{11.5}$$

$$m(2\dot{r}\dot{\theta} + r\ddot{\theta}) = 0 \tag{11.6}$$

The second or transverse equation, Eq. (11.6), gives the result that the angular momentum is 10 constant.

$$r^2\dot{\theta} = \text{constant} = L/m \tag{11.7}$$

where L is the angular momentum ( $\hbar$  in the case of the electron). The central force equations can be transformed into an orbital equation by the substitution,  $u = \frac{1}{r}$ . The differential equation of the orbit of a particle moving under a central force is

15 
$$\frac{\partial^2 u}{\partial \theta^2} + u = \frac{-1}{\underline{mL^2 u^2}} f(u^{-1})$$
 (11.8)

Because the angular momentum is constant, motion in only one plane need be considered; thus, the orbital equation is given in polar coordinates. The solution of Eq. (11.8) for an inverse-squared force

$$f(r) = -\frac{k}{r^2} \tag{11.9}$$

20 is

$$r = r_0 \frac{1+e}{1+e\cos\theta} \tag{11.10}$$

$$e = A - \frac{m\frac{L^2}{m^2}}{k} \tag{11.11}$$

$$r_0 = \frac{m\frac{L^2}{m^2}}{k(1+e)} \tag{11.12}$$

where e is the eccentricity of the ellipse and A is a constant. The equation of motion due to a central force can also be expressed in terms of the energies of the orbit. The square of the speed in polar coordinates is

$$v^2 = (\dot{r}^2 + r^2 \dot{\theta}^2) \tag{11.13}$$

5 Since a central force is conservative, the total energy, E, is equal to the sum of the kinetic, T, and the potential, V, and is constant. The total energy is

$$\frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2) + V(r) = E = \text{constant}$$
 (11.14)

Substitution of the variable  $u = \frac{1}{r}$  and Eq. (11.7) into Eq. (11.14) gives the orbital energy equation.

10 
$$\frac{1}{2}m\frac{L^2}{m^2}\left(\frac{\partial^2 u}{\partial \theta^2} + u^2\right) + V(u^{-1}) = E$$
 (11.15)

Because the potential energy function V(r) for an inverse-squared force field is

$$V(r) = -\frac{k}{r} = -ku \tag{11.16}$$

the energy equation of the orbit, Eq. (11.15),

$$\frac{1}{2}m\frac{L^2}{m^2}\left(\frac{\partial^2 u}{\partial \theta^2} + u^2\right) - ku = E \tag{11.17}$$

15 which has the solution

$$r = \frac{m\frac{L^2}{m^2}k^{-1}}{1 + \left(1 + 2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2}\cos\theta}$$
(11.18)

where the eccentricity, e, is

$$e = \left(1 + 2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2} \tag{11.19}$$

Eq. (11.19) permits the classification of the orbits according to the total energy, E, as 20 follows:

$$E < 0$$
,  $e < 1$  closed orbits (ellipse or circle)

 $E = 0$ ,  $e = 1$  parabolic orbit

 $E > 0$ ,  $e > 1$  hyperbolic orbit

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Since E = T + V and is constant, the closed orbits are those for which  $T \triangleleft V \mid$ , and the open orbits are those for which  $T \trianglerighteq \mid V \mid$ . It can be shown that the time average of the kinetic energy,  $\langle T \rangle$ , for elliptical motion in an inverse-squared field is 1/2 that of the time average of the magnitude of the potential energy,  $|\langle V \rangle|$ .  $|\langle T \rangle| = 1/2 |\langle V \rangle|$  [1].

As demonstrated in the One-Electron Atom section, the electric inverse-squared force is conservative; thus, the angular momentum of the electron,  $\hbar$ , and the energy of atomic orbitspheres are constant. In addition, the orbitspheres are nonradiative when the boundary condition is met.

The central force equation, Eq. (11.14), has orbital solutions, which are circular, 10 elliptical, parabolic, or hyperbolic. The former two types of solutions are associated with atomic and molecular orbitals. These solutions are nonradiative. The boundary condition for nonradiation given in the One-Electron Atom section, is the absence of components of the spacetime Fourier transform of the current-density function synchronous with waves traveling at the speed of light. The boundary condition is met when the velocity for the charge density 15 at every coordinate position on the orbitsphere is

$$v_n = \frac{\hbar}{m_e r_n} \tag{11.20}$$

The allowed velocities and angular frequencies are related to  $r_n$  by

$$v_n = r_n \omega_n \tag{11.21}$$

$$\omega_n = \frac{\hbar}{m_e r_n^2} \tag{11.22}$$

20 As demonstrated in the One-Electron Atom section and by Eq. (11.22), this condition is met for the product function of a radial Dirac delta function and a time harmonic function where the angular frequency,  $\omega$ , is constant and given by Eq. (11.22).

$$\omega_n = \frac{\hbar}{m_e r_n^2} = \frac{\frac{\pi L}{m_e}}{A} \tag{11.23}$$

where L is the angular momentum and A is the area of the closed orbit. Consider the solution of the central force equation comprising the product of a two-dimensional ellipsoid and a time harmonic function. The spatial part of the product function is the convolution of a radial Dirac delta function with the equation of an ellipsoid. The Fourier transform of the convolution of two functions is the product of the individual Fourier transforms of the functions; thus, the boundary condition is met for an ellipsoidal-time harmonic function when

$$\omega_n = \frac{\pi \hbar}{m A} = \frac{\hbar}{m ab} \tag{11.24}$$

where the area of an ellipse is

$$A = \pi ab \tag{11.25}$$

where b and 2b are the lengths of the semiminor and minor axes, respectively, and a and 2a are the lengths of the semimajor and major axes, respectively. The geometry of molecular hydrogen is ellipsoidal with the internuclear axis as the principal axis; thus, the electron orbital is a two-dimensional ellipsoidal-time harmonic function. The mass follows an elliptical path, time harmonically as determined by the central field of the protons at the foci. Rotational symmetry about the internuclear axis further determines that the orbital is a prolate of spheroid. In general, ellipsoidal orbits of molecular bonding, hereafter referred to as ellipsoidal molecular orbitals (MOs), have the general equation

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \tag{11.26}$$

The semiprincipal axes of the ellipsoid are a, b, c.

In ellipsoidal coordinates the Laplacian is

15 
$$(\eta - \zeta)R_{\xi} \frac{\partial}{\partial \xi} (R_{\xi} \frac{\partial \phi}{\partial \xi}) + (\zeta - \xi)R_{\eta} \frac{\partial}{\partial \eta} (R_{\eta} \frac{\partial \phi}{\partial \eta}) + (\xi - \eta)R_{\zeta} \frac{\partial}{\partial \zeta} (R_{\zeta} \frac{\partial \phi}{\partial \zeta}) = 0$$
 (11.27)

An ellipsoidal MO is equivalent to a charged perfect conductor (i.e. no dissipation to current flow) whose surface is given by Eq. (11.26). It is a two-dimensional equipotential membrane where each MO is supported by the outward centrifugal force due to the corresponding angular velocity, which conserves its angular momentum of  $\hbar$ . It satisfies the boundary conditions for a discontinuity of charge in Maxwell's equations, Eq. (11.48). It carries a total charge q = -e, and it's potential is a solution of the Laplacian in ellipsoidal coordinates, Eq. (11.27).

Excited states of orbitspheres are discussed in the Excited States of the One-Electron Atom (Quantization) section. In the case of ellipsoidal MOs, excited electronic states are created when photons of discrete frequencies are trapped in the ellipsoidal resonator cavity of the MO. The photon changes the effective charge at the MO surface where the central field is ellipsoidal and arises from the protons and the effective charge of the "trapped photon" at the foci of the MO. Force balance is achieved at a series of ellipsoidal equipotential two-dimensional surfaces confocal with the ground state ellipsoid. The "trapped photons" are solutions of the Laplacian in ellipsoidal coordinates, Eq. (11.27).

As is the case with the orbitsphere, higher and lower energy states are equally valid. The photon standing wave in both cases is a solution of the Laplacian in ellipsoidal coordinates. For an ellipsoidal resonator cavity, the relationship between an allowed circumference, 4aE, and the photon standing wavelength,  $\lambda$ , is

$$5 4aE = n\lambda (11.28)$$

where n is an integer and where the elliptic integral E of Eq. (11.28) is given by

$$E(k) = \int_{0}^{\frac{\pi}{2}} \sqrt{1 - k \sin^2 \phi} d\phi \tag{11.29}$$

$$k = e = \frac{\sqrt{a^2 - b^2}}{a} \tag{11.30}$$

Applying Eqs. (11.28) and (11.29-11.30), the relationship between an allowed angular 10 frequency given by Eq. (11.24) and the photon standing wave angular frequency,  $\omega$ , is:

$$\frac{\pi \hbar}{m_e A} = \frac{\hbar}{m_e n a_1 n b_1} = \frac{\hbar}{m_e a_n b_n} = \frac{1}{n^2} \omega_1 = \omega_n$$
 (11.31)

where n = 1, 2, 3, 4, ...

$$n = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots$$

 $\omega_i$  is the allowed angular frequency for n=1

15  $a_1$  and  $b_1$  are the allowed semimajor and semiminor axes for n=1

The potential,  $\phi$ , and distribution of charge,  $\sigma$  over the conducting surface of an ellipsoidal MO are sought given the conditions: 1.) the potential is equivalent to that of a charged ellipsoidal conductor whose surface is given by Eq. (11.26), 2.) it carries a total charge q = -e, and 3.) initially there is no external applied field. To solve this problem, a 20 potential function must be found which satisfies Eq. (11.27), which is regular at infinity, and which is constant over the given ellipsoid. The solution is well known and is given after Stratton [2]. Consider that the Laplacian is solved in ellipsoidal coordinates wherein  $\xi$  is the parameter of a family of ellipsoids all confocal with the standard surface  $\xi = 0$  whose axes have the specified values a, b, c. The variables  $\zeta$  and  $\eta$  are the parameters of confocal 25 hyperboloids and as such serve to measure position on any ellipsoid  $\xi = \text{constant}$ . On the surface  $\xi = 0$ ; therefore,  $\phi$  must be independent of  $\zeta$  and  $\eta$ . Due to the uniqueness property of solutions of the Laplacian, a function which satisfies Eq. (11.27), behaves

properly at infinity, and depends only on  $\xi$ , can be adjusted to represent the potential correctly at any point outside the ellipsoid  $\xi = 0$ .

Thus, it is assumed that  $\phi = \phi(\xi)$ . Then, the Laplacian reduces to

$$\frac{\partial}{\partial \xi} (R_{\xi} \frac{\partial \phi}{\partial \xi}) = 0 \qquad R_{\xi} = \sqrt{(\xi + a^2)(\xi + b^2)(\xi + c^2)}$$
 (11.32)

5 which on integration leads to

$$\phi(\xi) = C_1 \tilde{\xi} \frac{\partial \xi}{R_E} \tag{11.33}$$

where  $C_1$  is an arbitrary constant. The upper limit is selected to ensure the proper behavior at infinity. When  $\xi$  becomes very large,  $R_{\xi}$  approaches  $\xi^{3/2}$  and

$$\phi \sim \frac{2C_1}{\sqrt{\xi}} \tag{$\xi \to \infty$}$$

10 Furthermore, the equation of an ellipsoid can be written in the form

$$\frac{x^2}{1+\frac{\alpha^2}{\xi}} + \frac{y^2}{1+\frac{b^2}{\xi}} + \frac{z^2}{1+\frac{c^2}{\xi}} = \xi$$
 (11.35)

If  $r^2 = x^2 + y^2 + z^2$  is the distance from the origin to any point on the ellipsoid  $\xi$ , it is apparent that as  $\xi$  becomes very large  $\xi \to r^2$ . Thus, at great distances from the origin, the potential becomes that of a point charge at the origin:

$$15 \qquad \phi \sim \frac{2C_1}{r} \tag{11.36}$$

The solution Eq. (11.33) is, therefore, regular at infinity, and the constant  $C_1$  is then determined. It has been shown by Stratton [2] that whatever the distribution, the dominant term of the expansion at remote points is the potential of a point charge at the origin equal to the total charge of the distribution—in this case q. Hence  $C_1 = \frac{q}{8\pi\varepsilon_o}$ , and the potential at

20 any point is

$$\phi(\xi) = \frac{q}{8\pi\varepsilon_o} \int_{\xi}^{\infty} \frac{\partial \xi}{R_{\xi}} \tag{11.37}$$

The equipotential surfaces are the ellipsoids  $\xi = \text{constant}$ . Eq. (11.37) is an elliptic integral and its values have been tabulated [3].

Since the distance along a curvilinear coordinate  $u^1$  is measured not by  $du^1$  but by  $h_1du^1$ , the normal derivative in ellipsoidal coordinates is given by

$$\frac{\partial \phi}{\partial n} = \frac{1}{h_1} \frac{\partial \phi}{\partial \xi} = \frac{-q}{4\pi\varepsilon_o} \frac{1}{\sqrt{(\xi - \eta)(\xi - \zeta)}}$$
(11.38)

where

$$h_{1} = \frac{1}{2} \frac{\sqrt{(\xi - \eta)(\xi - \zeta)}}{R_{\varepsilon}}$$
 (11.39)

The density of charge,  $\sigma$ , over the surface  $\xi = 0$  is

$$\sigma = \varepsilon_o \left(\frac{\partial \phi}{\partial n}\right)_{\xi=0} = \frac{q}{4\pi\sqrt{\eta\zeta}} \tag{11.40}$$

Defining x, y, z in terms of  $\xi$ ,  $\eta$ ,  $\zeta$  we put  $\xi = 0$ , it may be easily verified that

$$\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4} = \frac{\zeta \eta}{a^2 b^2 c^2}$$
 (\xi = 0)

10 Consequently, the charge density in rectangular coordinates is

$$\sigma = \frac{q}{4\pi abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$
(11.42)

(The mass-density function of an MO is equivalent to its charge-density function where m replaces q of Eq. (11.42)). The equation of the plane tangent to the ellipsoid at the point  $x_0, y_0, z_0$  is

15 
$$X \frac{x_0}{a^2} + Y \frac{y_0}{b^2} + Z \frac{z_0}{c^2} = 1$$
 (11.43)

where X, Y, Z are running coordinates in the plane. After dividing through by the square root of the sum of the squares of the coefficients of X, Y, and Z, the right member is the distance D from the origin to the tangent plane. That is,

$$D = \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$
 (11.44)

20 so that for an electron MO

$$\sigma = \frac{-e}{4\pi abc}D\tag{11.45}$$

In other words, the surface density at any point on a charged ellipsoidal conductor is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin.

In the case of hydrogen-type molecules and molecular ions, rotational symmetry about the internuclear axis requires that two of the axes be equal. Thus, the MO is a spheroid, and 5 Eq. (11.37) can be integrated in terms of elementary functions. If a > b = c, the spheroid is prolate, and the potential is given by

$$\phi = \frac{1}{8\pi\varepsilon_o} \frac{-e}{\sqrt{a^2 - b^2}} \ln \frac{\sqrt{\xi + a^2} + \sqrt{a^2 - b^2}}{\sqrt{\xi + a^2} - \sqrt{a^2 - b^2}}$$
(11.46)

#### SPHEROIDAL FORCE EQUATIONS

10

#### **Electric Force**

The spheroidal MO is a two-dimensional surface of constant potential given by Eq. (11.46) for  $\xi = 0$ . For an isolated electron MO the electric field inside is zero as given by Gauss' Law

$$\int_{S} \mathbf{E} dA = \int_{V} \frac{P}{\varepsilon_{0}} dV \tag{11.47}$$

15 where the charge density,  $\rho$ , inside the MO is zero. Gauss' Law at a two-dimensional surface with continuity of the potential across the surface according to Faraday's law in the electrostatic limit [4-6] is

$$\mathbf{n} \bullet (\mathbf{E}_1 - \mathbf{E}_2) = \frac{\sigma}{\varepsilon_0} \tag{11.48}$$

 $E_2$  is the electric field inside which is zero. The electric field of an ellipsoidal MO with 20 semimajor and semiminor axes a and b=c, respectively, is given by substituting  $\sigma$  given by Eq. (11.38-11.42) into Eq. (11.48).

$$\mathbf{E} = \frac{\sigma}{\varepsilon_o} \mathbf{i}_{\xi} = \frac{-e}{4\pi\varepsilon_o} \frac{1}{\sqrt{(\xi - \eta)(\xi - \zeta)}} \mathbf{i}_{\xi} = \frac{-e}{4\pi\varepsilon_o abc} D \mathbf{i}_{\xi} = \frac{-e}{4\pi\varepsilon_o abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_{\xi}$$

(11.49)

wherein the ellipsoidal-coordinate parameter  $\xi = 0$  at the surface of the MO and D is the 25 distance from the origin to the tangent plane given by Eq. (11.44). The electric field and thus the force and potential energy between the protons and the electron MO can be solved based on three principles: (1) Maxwell's equations require that the electron MO is a equipotential energy surface that is a function of  $\xi$  alone; thus, it is a prolate spheroid, (2) stability to

radiation, and conservation first principles require that the angular velocity is constant and given in polar coordinates with respect to the origin by Eq. (11.24), and (3) the equations of motion due to the central force of each proton (Eqs. (11.5-11.19) and Eqs. (11.68-11.70)) also determine that the current is ellipsoidal, and based on symmetry, the current is a prolate spheroid. Thus, based on Maxwell's equations, conservation principles, and Newton's Laws for the equations of motion, the electron MO constraints and the motion under the force of the protons both give rise to a prolate spheroid. Since the energy of motion is determined from the Coulombic central field (Eqs. (11.5-11.19), the protons give rise to a prolate spheroidal energy surface (a surface of constant energy) that is matched to the equipotential, prolate spheroidal electron MO.

The force balance equation between the protons and the electron MO is solved to give the position of the foci, then the total energy is determined including the repulsive energy between the two protons at the foci to determine whether the original assumption of an elliptic orbit was valid. If the condition that E < 0 is met, then the problem of the stable elliptic orbit is solved. In any case that this condition is not found to be met, then a stable orbit can not be formed.

The force and energy equations of a point charge(mass) (Eqs. (11.5-11.24)) are reformulated in term of densities for charge, current, mass, momentum, and potential, kinetic, and total energies. Consider an elliptical orbit shown in Figure 1 that applies to a point 20 charge(mass) as well as a point on a continuous elliptical current loop that comprises a basis element of the continuous current density of the ellipsoidal MO. The tangent plane at any point on the ellipsoid makes equal angles with the foci radii at that point and the sum of the distance to the foci is a constant, 2a. Thus, the normal is the bisector of the angle between the foci radii at that point as shown in Figure 1.

The unit vector normal to the ellipsoidal MO at a point (x, y, z) is

$$\hat{\mathbf{d}} = \frac{\left(\frac{x}{a^2}, \frac{y}{b^2}, \frac{z}{b^2}\right)}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$
(11.50)

 $F_1(r(t))$  and  $F_2(r(t))$  are defined as the components of the central forces centered on  $F_1$  and  $F_2$ . The components of the central forces that are normal to the ellipsoidal MO in the direction of  $\hat{\mathbf{d}}$ , the unit vector in the  $\mathbf{i}_{\xi}$ -direction are defined as  $F_{11}(r(t))$  and  $F_{21}(r(t))$ .

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The normalized projections or projection factor of the sum of these central forces in the  $\hat{\mathbf{d}}$ -direction at the point (x, y, z) is

$$\frac{F_{1\perp}(r(t)) + F_{2\perp}(r(t))}{|F_{1}(r(t)) + F_{2}(r(t))|} = \frac{(\mathbf{r}_{1} + \mathbf{r}_{2}) \cdot \hat{\mathbf{d}}}{2a}$$

$$= \frac{((x - c, y, z) + (x - c, y, z)) \cdot \left(\frac{x}{a^{2}} + \frac{y}{b^{2}} + \frac{z}{b^{2}}\right)}{2a\sqrt{\frac{x^{2}}{a^{4}} + \frac{y^{2}}{b^{4}} + \frac{z^{2}}{c^{4}}}}$$

$$= \frac{\left(\frac{x^{2} - cx}{a^{2}} + \frac{y^{2}}{b^{2}} + \frac{z^{2}}{b^{2}}\right) + \left(\frac{x^{2} + cx}{a^{2}} + \frac{y^{2}}{b^{2}} + \frac{z^{2}}{b^{2}}\right)}{2a\sqrt{\frac{x^{2}}{a^{4}} + \frac{y^{2}}{b^{4}} + \frac{z^{2}}{c^{4}}}}$$

$$= \frac{1}{a\sqrt{\frac{x^{2}}{a^{4}} + \frac{y^{2}}{b^{4}} + \frac{z^{2}}{c^{4}}}}$$
(11.51)

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the radial vectors of the central forces from the corresponding focus to 5 the point (x, y, z) on the ellipsoidal MO.

The polar-coordinate elliptical orbit of a point charge due to its motion in a central inverse-squared-radius field is given by Eqs. (11.10-11.12) as the solution of the polar-coordinate-force equations, Eqs. (11.5-11.19) and (11.68-11.70). The orbit is also completely specified in Cartesian coordinates by the solution of Eqs. (11.5-11.19) and (11.68-11.70) for the semimajor and semiminor axes. Then, the corresponding polar-coordinate elliptical orbit is given as a plane cross section through the foci of the Cartesian-coordinate-system ellipsoid having the same axes given by Eq. (11.26) where c = b. Thus, the Columbic central force can be determined in terms of the general Cartesian coordinates from the polar-coordinate central force equations (Eqs. (11.5-11.19)). Consider separately the elliptical solution at each focus given in polar coordinates by Eq. (11.10):

$$r_i = a(1-e)\frac{1+e}{1+e\cos\theta} = \frac{a(1-e^2)}{1+e\cos\theta}$$
 (11.52)

$$r_2 = \frac{a(1-e^2)}{1+e\cos(\theta+\pi)} = \frac{a(1-e^2)}{1-e\cos\theta}$$
 (11.53)

where

$$r_0 = a - c' = a \left( 1 - \frac{c'}{a} \right) = a \left( 1 - e \right)$$
 (11.54)

The magnitude of the sum of the central forces centered on  $F_1$  and  $F_2$  that are normal to the ellipsoidal MO are

$$|F_{1}(r_{1})| + |F_{2}(r_{2})| = \frac{k}{r_{1}^{2}} + \frac{k}{r_{2}^{2}}$$

$$= k \frac{(1 + e \cos \theta)^{2} + (1 - e \cos \theta)^{2}}{a^{2} (1 - e^{2})^{2}}$$

$$= k \frac{1 + 2e \cos \theta + e^{2} \cos^{2} \theta + 1 - 2e \cos \theta + e^{2} \cos^{2} \theta}{a^{2} (1 - e^{2})^{2}}$$

$$= k \frac{1 + e^{2} \cos^{2} \theta + 1 + e^{2} \cos^{2} \theta}{a^{2} (1 - e^{2})^{2}}$$

$$= k \frac{2 + 2e^{2} \cos^{2} \theta}{a^{2} (1 - e^{2})^{2}}$$

$$= k \frac{2 + 2e^{2} \cos^{2} \theta}{a^{2} (1 - e^{2})^{2}}$$
(11.55)

The vector central forces centered on  $F_1$  and  $F_2$  that are normal to the ellipsoidal MO are 5 then given by the product of the corresponding magnitude and vector projection given by Eqs. (11.55) and (11.51), respectively:

$$\mathbf{F}_{1\perp}(r_1) + \mathbf{F}_{2\perp}(r_2) = k \frac{2 + 2e^2 \cos^2 \theta}{a^2 (1 - e^2)^2} \frac{1}{a \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_{\xi}$$
(11.56)

Eq. (11.56) is based on a single point charge e. For a charge-density distribution that is given as an ellipsoidal equipotential, the  $\theta$ -dependence must vanish. In addition to the elliptical orbit being completely specified in Cartesian coordinates by the solution of Eqs. (11.5-11.19) and Eqs. (11.68-11.70) for the semimajor and semiminor axes in Eq. (11.26), the polar-coordinate elliptical orbit is also completely specified by the total constant total energy E and the angular momentum which for the electron is the constant  $\hbar$ . Considering Eq. (11.56), the corresponding total energy of the electron is conserved and is determined by the integration over the MO to give the average:

$$\mathbf{F}_{1\perp}(r_1) + \mathbf{F}_{2\perp}(r_2) = k \frac{2 + e^2}{a^2 (1 - e^2)^2} \frac{1}{a \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_{\xi}$$
(11.57)

Eq. (11.57) is transformed from a two-centered-central force to a one-centered-central force to match the form of the potential of the ellipsoidal MO. In this case,

$$\mathbf{r}_{1}, \mathbf{r}_{2} \to r(t)\mathbf{i}_{\xi} \tag{11.58}$$

20 In the case that

$$r_1 = r_2 = a \tag{11.59}$$

then,

5

$$r(t) = b (11.60)$$

and the one-centered-central force is in the  $i_{\xi}$ -direction. Thus, Eq. (11.57) transforms as

$$\mathbf{F}_{1\perp}(r(t)) + \mathbf{F}_{2\perp}(r(t)) = k \frac{\left(1 - e^2\right)^2}{b^2 \left(2 + e^2\right)} \frac{1}{a\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$

$$= \frac{2 + e^2}{\left(1 - e^2\right)^2} k \frac{1}{ab^2 \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_{\xi}$$
(11.61)

Eq. (11.61) has the same form as that of the electric field of the ellipsoidal MO given by Eq. (11.49), except for the scaling factor of two-centered coordinates  $h_{2cc}$ :

$$h_{2cc} = \frac{2 + e^2}{\left(1 - e^2\right)^2} \tag{11.62}$$

As shown in the case of the derivation of the Laplacian charge-density and electric field, if  $r^2 = x^2 + y^2 + z^2$  is the distance from the origin to any point on the ellipsoid  $\xi$ , it is apparent that as  $\xi$  becomes very large  $\xi \to r^2$ . Thus, at great distances from the origin, the potential becomes that of a point charge at the origin as given by Eq. (11.36). The same boundary condition applies to the potential and field of the protons. The limiting case is also given as  $e \to 0$ . Then, to transform the scale factor to that of one-centered coordinates for an ellipsoidal MO, the reciprocal of the scaling factor multiplies the Laplacian-MO-electric-field term. The reciprocal of Eq. (11.62) is

$$h_{2cc}^{-1} = \frac{\left(1 - e^2\right)^2}{2 + e^2} \tag{11.63}$$

such that as  $e \to 0$ ,  $h_{2cc}^{-1} \to \frac{1}{2}$ . This transform scale factor corresponds to the interchange of the points of highest and lowest velocity on the surface and the distribution of the charge-20 density in the opposite manner as shown *infra*. The charge-density distribution corrects the angular variation in central force over the surface such that a solution of the central force equation of motion and the Laplacian MO are solved simultaneously. It can also be considered as a multipole normalization factor such those of the spherical harmonics and the

spherical geometric factor of atomic electrons that gives the central force as a function of  $\xi$  only.

The reciprocal of the  $h_{2cc}$  form-factor with the dependence of the charge density on the distance parameter r(t) gives

5 
$$\mathbf{F}_{1\perp}(r(t)) + \mathbf{F}_{2\perp}(r(t)) = k \frac{(1 - e^2)^2}{b^2 (2 + e^2)} \frac{1}{a \sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_{\xi}$$
 (11.64)

From Eq. (11.31), the magnitude of the ellipsoidal field corresponding to a below "ground state" hydrogen-type molecular ion is an integer p. The integer is one in the case of the hydrogen molecular ion and an integer greater than one in the case of each dihydrino molecular ion. The central-electric-force constant, k, from the two protons that includes the central-field contribution due photons of lower-energy states is

$$k = \frac{Ze^2}{4\pi\varepsilon_0} = \frac{p2e^2}{4\pi\varepsilon_0} \tag{11.65}$$

Substitution of Eq. (11.65) for k in Eq. (11.64) gives the one-center-coordinate electric force  $\mathbf{F}_{els}$  between the protons and the ellipsoidal MO:

$$\mathbf{F}_{ele} = \mathbf{F}_{11}(r(t)) + \mathbf{F}_{21}(r(t)) = \frac{2pe^2}{4\pi\varepsilon_0} \frac{\left(1 - \left(\frac{c'}{a}\right)^2\right)^2}{ab^2 \left(2 + \left(\frac{c'}{a}\right)^2\right)} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \mathbf{i}_{\xi}$$
(11.66)

15 where e is the charge and with the distance from the origin to a nucleus at a focus defined as e, the eccentricity, e, is

$$e = \frac{c'}{a} \tag{11.67}$$

From the orbital equations in polar coordinates, Eqs. (11.10-11.12), the following relationship can be derived [1]:

$$20 a = \frac{m\frac{L^2}{m^2}}{k(1-e^2)} (11.68)$$

For any ellipse,

$$b = a\sqrt{1 - e^2} \tag{11.69}$$

Thus,

$$b = a\sqrt{\frac{L^2}{m^2} \frac{m}{ka}}$$
 (point charge (mass) in polar coordinates) (11.70)

From, the equal energy condition, it can be shown that b for the motion of a point charge (mass) in polar coordinates due to a proton at one focus corresponds to

$$c' = \sqrt{a^2 - b^2} \tag{11.71}$$

5 of the MO in ellipsoidal coordinates, and  $k_1$  of one attracting focus is replaced by  $k = 2k_1$  of ellipsoidal coordinates with two attracting foci. In ellipsoidal coordinates, k is given by Eq. (11.65) and L for the electron equals  $\hbar$ .

Consider the force balance equation for the point on the ellipse at the intersection of the semiminor axis b with the ellipse. At this point called (0,b), the distances from each 10 focus,  $r_1$  and  $r_2$ , to the ellipse are equal. The relationship for the sum of the distances from the foci to any point on the ellipse is

$$r_1 + r_2 = 2a ag{11.72}$$

Thus, at point (0,b),

$$r_1 = r_2 = a \tag{11.73}$$

15 Using Eq. (11.5), the magnitude of the force balance in the radial (r(t)) direction, from the origin, is given by

$$mr\dot{\theta}^2 = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\sin\theta = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\frac{b}{a}$$
 (11.74)

wherein the  $m\ddot{r}$  term is zero and  $\theta$  is the angle from the focus to point (0,b). Using Eqs. (11.24), (11.94), and (11.95), Eq. (11.74) becomes

$$mr\omega^{2} = mb \frac{\hbar^{2}}{m^{2}a^{2}b^{2}} = \frac{2pe^{2}}{4\pi\varepsilon_{0}a^{2}} \frac{b}{a}$$
 (11.75)

In order for the prolate spheroidal MO to be an equipotential surface, the mass and charge density must be according to Eq. (11.45). In this case, the mass and charge density along the ellipse is such that the magnitudes of the radial and transverse forces components at point (0,b) are equivalent. Furthermore, according to Eq. (11.5), the central force of each proton at a focus is separable and symmetrical to that at the other focus. Based on symmetry, the transverse forces of the two protons are in opposite directions and the radial components are in the same direction. But, the relationship between the magnitudes must still hold wherein at

point (0,b) the transverse force is equivalent to that due to the sum of the charges at one focus. The sum of the magnitudes of the transverse forces which is equivalent to a force of 2e at each focus in turn is

$$\left| f(r)e_{\theta} \right| = \frac{2pe^2}{4\pi\varepsilon_0 a^2} \cos\theta = \frac{2pe^2}{4\pi\varepsilon_0 a^2} \frac{c'}{a}$$
 (11.76)

5 Thus, using the mass and charge-density scaling factor,  $\frac{\frac{c'}{a}}{\frac{b}{a}} = \frac{c'}{b}$ , to match the equipotential

condition in Eq. (75) gives

$$b\frac{\hbar^2}{m_e \frac{c'}{b}a^2b^2} = \frac{2\frac{c'}{b}pe^2}{4\pi\varepsilon_0 a^2}\frac{b}{a}$$
 (11.77)

$$c^{2} = \frac{\hbar^2 4\pi \varepsilon_0 a}{m_e 2pe^2} \tag{11.78}$$

Using Eq. (1.235)

10

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{me^2 2pa}} = \sqrt{\frac{aa_0}{2p}} \tag{11.79}$$

Then, the length of the semiminor axis of the prolate spheroidal MO, b=c, is

$$b = \sqrt{a^2 - c'^2} \tag{11.80}$$

Correspondingly, c' is given by Eq. (11.71).

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Substitution of Eq. (11.79) into Eq. (11.66) gives the electric force:

$$\mathbf{F}_{ele} = \frac{2pe^{2}}{4\pi\varepsilon_{0}} \frac{\left(1 - \left(\frac{\sqrt{\frac{aa_{0}}{2p}}}{a}\right)^{2}\right)^{2}}{ab^{2}\left(2 + \left(\frac{\sqrt{\frac{aa_{0}}{2p}}}{a}\right)^{2}\right)\sqrt{\frac{x^{2}}{a^{4}} + \frac{y^{2}}{b^{4}} + \frac{z^{2}}{c^{4}}}} \mathbf{i}_{\xi}$$

$$= \frac{2pe^{2}}{4\pi\varepsilon_{0}} \frac{\left(1 - \frac{a_{0}}{2ap}\right)^{2}}{ab^{2}\left(2 + \frac{a_{0}}{2ap}\right)\sqrt{\frac{x^{2}}{a^{4}} + \frac{y^{2}}{b^{4}} + \frac{z^{2}}{c^{4}}}} \mathbf{i}_{\xi}$$

$$= \frac{2pe^{2}}{4\pi\varepsilon_{0}} \frac{\left(1 - \frac{a_{0}}{2ap}\right)^{2}}{ab^{2}\left(2 + \frac{a_{0}}{2ap}\right)} D\mathbf{i}_{\xi}$$
(11.81)

#### Centrifugal Force

5 The centrifugal force along the radial vector from each proton at each focus of the ellipsoid is given by the  $mr\dot{\theta}^2$  term of Eq. (11.5). The tangent plane at any point on the ellipsoid makes equal angles with the foci radii at that point and the sum of the distance to the foci is a constant, 2a. Thus, the normal is the bisector of the angle between the foci radii at that point as shown in Figure 1. In order to satisfy the equation of motion for an equal energy surface 10 for both foci, the transverse component of the central force of one foci at any point on the elliptic orbit due to the central force of the other (Eq. (11.5)) must cancel on average and vice Thus, the centrifugal force due to the superposition of the central forces in the direction of each foci must be normal to an ellipsoidal surface in the direction perpendicular to the direction of motion. Thus, it is in the  $\xi$ -direction. This can be only be achieved by a 15 time rate of change of the momentum density that compensates for the variation of the distances from each focus to each point on an elliptical cross section. Since the angular momentum must be conserved, there can be no net force in the direction transverse to the elliptical path over each orbital path. The total energy must also be conserved; thus, as shown infra. the distribution of the mass must also be a solution of Laplace's equation in the 20 parameter  $\xi$  only. Thus, the mass-density constraint is the same as the charge-density constraint. As further shown infra., the distribution and concomitantly the centrifugal force is

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a function of D, the time-dependent distance from the center of the ellipsoid to a tangent plane given by Eq. (11.44) where D and the Cartesian coordinates are the time-dependent parameters.

Each point or coordinate position on the continuous two-dimensional electron MO 5 defines an infinitesimal mass-density element which moves along an orbit comprising an elliptical plane cross section of the spheroidal MO through the foci. The kinetic energy of the electron is conserved. Then, the corresponding radial conservative force balance equation is

$$m(\ddot{r} + C_1 r) = 0 (11.82)$$

The motion is such that eccentric angle,  $\theta$ , changes at a constant rate at each point. That is  $10 \theta = \omega t$  at time t where the angular velocity  $\omega$  is a constant. The solution of the homogeneous equation with  $C_1 = \omega^2$  is

$$r(t) = ia\cos\omega t + jb\sin\omega t \tag{11.83}$$

where a is the semimajor axis, b is semiminor axis, and the boundary conditions of r(t) = a

for  $\omega t = 0$  and r(t) = b for  $\omega t = \frac{\pi}{2}$  were applied. Eq. (11.83) is the parametric equation of

15 the ellipse of the orbit. The velocity is given by the time derivative of the parametric position vector:

$$v(t) = \dot{r}(t) = -\mathbf{i}a\omega\sin\omega t + \mathbf{j}b\omega\cos\omega t \tag{11.84}$$

The velocity is  $\frac{\pi}{2}$  out of phase with the charge density at r(t) = a ( $\omega t = 0$ ) and r(t) = b

 $(\omega t = \frac{\pi}{2})$  such that the lowest charge density has the highest velocity and the highest charge

20 density has the lowest velocity. In this case, it can be shown that the current is constant along each elliptical path of the MO. Recall that nonradiation results when  $\omega$  = constant given by Eq. (11.24) that corresponds to a constant current, which further maintains the current continuity condition.

Consider Eq. (11.32) for the prolate spheroidal MO. From this equation, the mass and current-densities, the angular momentum, and the potential and kinetic energies are a function of  $\xi$  alone, and any dependence on the orthogonal coordinate parameters averages to unity. From Eq. (11.32),

$$R_{\xi} \frac{\partial \phi}{\partial \xi} = C_1 \tag{11.85}$$

Substitution of Eq. (11.40) into Eq. (11.85) gives

$$\int_{\xi}^{\infty} R_{\xi} h_{1} \frac{e}{4\pi\sqrt{\eta \zeta}} \delta(\xi) d\xi = \varepsilon_{0} C_{1} = \frac{e}{8\pi}$$
(11.86)

where  $C_1$  is from Eq. (11.36). Substitution of Eq. (11.39) into Eq. (11.86) gives

$$\int_{\xi}^{\infty} R_{\xi} \frac{e}{4\pi\sqrt{\eta\zeta}} \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_{\xi}} \delta(\xi) d\xi = \frac{e}{8\pi}$$
(11.87)

Comparison of Eq. (11.86) with Eq. (11.87) demonstrates that the

$$8\pi \int_{\xi}^{\infty} R_{\xi} \frac{e}{4\pi\sqrt{\eta\zeta}} \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_{\xi}} \delta(\xi) d\xi = e$$
 (11.88)

The current density J is given by the product of the constant frequency (Eq. (11.24)) and the charge density (Eq. (11.40)):

$$J = \frac{\hbar}{2\pi m_e ab} \frac{e}{4\pi \sqrt{\eta \zeta}} \tag{11.89}$$

The total constant current is dependent on  $\xi$  alone according to Eq. (11.32). Then, applying 10 the result of Eq. (11.88) to Eq. (11.89) gives

$$\mathbf{i} = 8\pi \int_{\xi}^{\infty} R_{\xi} \frac{\hbar}{2\pi m_{e} ab} \frac{e}{4\pi \sqrt{\eta \zeta}} \frac{1}{2} \frac{\sqrt{(\xi - \eta)(\xi - \zeta)}}{R_{\xi}} \delta(\xi) d\xi \, \mathbf{e}_{\zeta} \times \mathbf{e}_{\xi} = \frac{e\hbar}{2\pi m_{e} ab} \, \mathbf{e}_{\eta} \quad (11.90)$$

the constant current that is nonradiative.

If  $\mathbf{a}(t)$  denotes the acceleration vector, then

$$\mathbf{a}(t) = -\omega^2 r(t)\mathbf{i},\tag{11.91}$$

In other words, the acceleration is centrifugal as in the case of circular motion with constant angular speed  $\omega$ . The dot product of  $\mathbf{r}(t)$  with  $\hat{\mathbf{d}}$ , the unit vector normal to the ellipsoidal MO at a point (x, y, z) given by Eq. (11.50), is

$$\mathbf{r}(t) \cdot \hat{\mathbf{d}} = \frac{(x, y, z) \cdot \left(\frac{x}{a^2}, \frac{y}{b^2}, \frac{z}{b^2}\right)}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} = \frac{\left(\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{b^2}\right)}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$
(11.92)

Using Eq. (11.26), the normal component projection is

20 
$$\mathbf{r}(t) \cdot \hat{\mathbf{d}} = \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} = D$$
 (11.93)

where D, the distance from the origin to the tangent plane, is given by Eq. (11.44).

The centrifugal force,  $\mathbf{F}_{cl}$ , on mass element  $m_l$  [7] given by the second term of Eq. (11.82) is

$$\mathbf{F}_{cl} = m_i a = -m_i \omega^2 r(t) \tag{11.94}$$

Substitution of the angular velocity given by Eq. (11.24) and  $m_e$  for m into Eq. (11.94) gives the centrifugal force  $\mathbf{F}_e$  on the electron that is normal to the MO surface according to Eq. (11.93):

$$\mathbf{F}_{c} = \frac{-\hbar^{2}}{m_{e}a^{2}b^{2}}\mathbf{r}\left(t\right)\cdot\hat{\mathbf{d}}\mathbf{i}_{\xi} = \frac{-\hbar^{2}}{m_{e}a^{2}b^{2}}D\mathbf{i}_{\xi} \tag{11.95}$$

 $\mathbf{F}_c$  has an equivalent dependence on D as the electric force based on the charge distribution (Eq. (11.45)). This is expected based on the invariance of  $\frac{e}{m_e}$  which results in the same 10 distribution of the mass and charge.

The equipotential charge-density distribution gives rise to the constant current condition. It also gives rise to a constant total kinetic energy condition wherein the angular velocity given by Eq. (11.24) is a constant. Recall from Eq. (11.32), that on the surface  $\xi = 0$ ;  $\phi$  must be independent of  $\zeta$  and  $\eta$  and depend only on  $\xi$  at any point outside the ellipsoid  $\xi = 0$ . Since the current and total kinetic energy are also constant on the surface  $\xi = 0$ , the total kinetic energy depends only on  $\xi$ . Thus, the centrifugal force on the mass of the electron,  $m_e$ , must be in the same direction as the electric field corresponding to  $\phi$ , normal to the electron surface wherein any tangential component in Eq. (11.94) averages to zero over the electron MO by the mass distribution given by Eqs. (11.40) and (11.45) with  $m_e$  replacing e.

The cancellation of tangential acceleration over each elliptical path maintains the charge density distribution given by Eq. (11.40) with constant current at each point on each elliptical path of the MO. Since the centrifugal force is given by Eq. (11.94), the multiplication of the mass density by the scaling factor  $h_1$  and integration with respect to  $\xi$  gives a constant net centrifugal force. Thus, the result matches those of the determination of the constant current (Eq. (11.90)) and angular momentum shown *infra*. (Eq. (11.101)) wherein the charge and mass densities given in Eqs. (11.90-11.91) and (11.100), respectively, were integrated over.

Specifically, consider the normal-directed centrifugal force,  $\mathbf{F}_{ci}$ , on mass element  $m_i$ :

$$\mathbf{F}_{ci} = -m_i \omega^2 D \mathbf{i}_{c} \tag{11.96}$$

The mass density is given by Eq. (11.40) with  $m_e$  replacing e. Then, the substitution of the mass density for  $m_i$  in Eq. (11.96) and using Eq. (11.24) for  $\omega$  gives the centrifugal force density  $\mathbf{F}_{\infty}$ :

5 
$$\mathbf{F}_{ca} = \frac{m_e}{4\pi\sqrt{\eta\zeta}} \frac{\hbar^2}{m_e^2 a^2 b^2} D\mathbf{i}_{\xi}$$
 (11.97)

Eq. (11.32) determines that the centrifugal force is a function of  $\xi$  alone, and any dependence on the transverse coordinate parameters averages to zero. Using the result of Eq. (11.88) gives the net centrifugal force  $\mathbf{F}_{\epsilon}$ :

$$\mathbf{F}_{c} = 8\pi \int_{\xi}^{\infty} \frac{1}{4\pi\sqrt{\eta\zeta}} \frac{\hbar^{2}}{m_{e}a^{2}b^{2}} R_{\xi} \frac{1}{2} \frac{\sqrt{(\xi - \eta)(\xi - \zeta)}}{R_{\xi}} D\delta(\xi) d\xi \mathbf{i}_{\xi} = \frac{\hbar^{2}}{m_{e}a^{2}b^{2}} D\mathbf{i}_{\xi}$$
(11.98)

In the limit as the ellipsoidal coordinates go over into spherical coordinates, Eq. (11.95) reduces to the centrifugal force of the spherical orbitsphere given by Eq. (1.232) with Eq. (1.47). This condition must be and is met as a further boundary condition that parallels that of Eqs. (11.32-11.37). Using the same dependence of the total mass(charge) on the scale factor  $h_1$  according to Eqs. (11.32-11.40), the further boundary conditions on the angular momentum and kinetic energy are met.

Specifically, the constant potential and current conditions and the use of Eq. (11.32) in the derivation of Eq. (11.95) also satisfy another condition, the conservation of  $\hbar$  of angular momentum of the electron. The angular momentum  $\mathbf{p}_i$  at each point i of mass  $m_i$  is

$$\mathbf{p}_{i}(t) = m_{i}\mathbf{r}(t) \times \mathbf{v}(t)$$

$$= m_{i}(\mathbf{i}a\cos\omega t + \mathbf{j}b\sin\omega t) \times (-\mathbf{i}a\omega\sin\omega t + \mathbf{j}b\omega\cos\omega t)$$

$$= m_{i}ab\omega(\cos^{2}\omega t + \sin^{2}\omega t)\mathbf{i} \times \mathbf{j}$$

$$= m_{i}ab\omega\mathbf{k}$$
(11.99)

20 The mass density is given by Eq. (11.40) with  $m_e$  replacing e. Then, substitution of  $m_i$  in Eq. (11.99) by the mass density and using Eq. (11.24) for  $\omega$  gives the angular momentum density  $\mathbf{p}(t)$ :

$$\mathbf{p}(t) = ab\omega \frac{m_e}{4\pi\sqrt{\eta\zeta}} \mathbf{k} = ab \frac{\hbar}{m_e ab} \frac{m_e}{4\pi\sqrt{\eta\zeta}} \mathbf{k}$$
 (11.100)

Using the result of Eq. (11.88) gives the total constant angular momentum L:

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$$\mathbf{L} = 8\pi \int_{\xi}^{\infty} \hbar \frac{1}{4\pi \sqrt{\eta \zeta}} R_{\xi} \frac{1}{2} \frac{\sqrt{(\xi - \eta)(\xi - \zeta)}}{R_{\xi}} \delta(\xi) d\xi \mathbf{k} = \hbar \mathbf{k}$$
 (11.101)

Eq. (11.101) demonstrates conservation of angular momentum that is a function of  $\xi$  alone that parallels the case of atomic electrons where L conservation is a function of the radius r alone as given by Eq. (1.57).

Similarly, the kinetic energy T(t) at each point i of mass  $m_i$  is

$$T(t) = \frac{1}{2} m_i v(t)^2$$

$$= \frac{1}{2} m_i \left( -\mathbf{i}a\omega \sin \omega t + \mathbf{j}b\omega \cos \omega t \right)^2$$

$$= \frac{1}{2} m_i \omega^2 \left( a^2 \sin^2 \omega t + b^2 \cos^2 \omega t \right)$$
(11.102)

In Eqs. (11.96-11.98),  $m_i$  was replaced by the mass density and the  $\xi$  integral was determined to give the centrifugal force in terms of the mass of the electron. The kinetic energy can also be determined from the  $\xi$  integral of the centrifugal force:

$$T = h_{2cc} F_c \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}}$$
 (11.103)

The result is given in Eq. (11.119). From Eq. (11.102), the kinetic energy is time (position) dependent, but the total kinetic energy corresponding to the centrifugal force given by Eq. (11.95) satisfies the condition that the time-averaged kinetic energy is 1/2 the time-averaged potential energy for elliptic motion in an inverse-squared central force [1]. (Here, the potential and total kinetic energies are constant and correspond to the time-averaged energies of the general case.) Thus, as shown by Eqs. (11.122) (11.124), (11.262), and (11.264) energy is conserved.

### Force Balance of Hydrogen-type Molecular Ions

20 Consider the case of spheroidal coordinates based on the rotational symmetry about the semimajor axis [2]. In the limit, as the focal distance 2c and the eccentricity of the series of confocal ellipses approaches zero, spheroidal coordinates go over into spherical coordinates with  $\xi \to r$  and  $\eta \to \cos \theta$ . The field of an equipotential two-dimensional charge surface of constant radius r = R is equivalent to that of a point charge of the total charge of the spherical shell at the origin. The force balance between the centrifugal force and the central Coulomb force for spherical symmetry is given by Eq. (1.232).

37

Similarly, the centrifugal force is the direction of  $\xi$  and balances the central Coulombic force between the protons at the foci and the electron MO. In the case of the prolate spheroidal MO, the inhomogeneous equation given by Eq. (11.5) must hold for each fixed position of r(t) since the MO is static in time due to the constant current condition.

5 With r(t) fixed, the  $m\ddot{r}$  term of Eq. (11.5) is zero, and the force balanced equation is the balance between the centrifugal force and the Coulombic force which are both normal to the surface of the elliptic orbit:

$$mr\dot{\theta}^2 = f(r) \tag{11.104}$$

Substitution of Eq. (11.81) and Eq. (11.95) into Eq. (11.104) gives the force balance between 10 the centrifugal and electric central forces:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{2pe^2}{4\pi\varepsilon_0} \frac{\left(1 - \frac{a_0}{2ap}\right)^2}{ab^2 \left(2 + \frac{a_0}{2ap}\right)} D \tag{11.105}$$

$$\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2ap} \left( 2 + \frac{a_0}{2ap} \right) = \left( 1 - \frac{a_0}{2ap} \right)^2 \tag{11.106}$$

$$\frac{a_0}{ap} + \left(\frac{a_0}{2ap}\right)^2 = \left(1 - \frac{a_0}{2ap}\right)^2 \tag{11.107}$$

$$\frac{a_0}{ap} + \left(\frac{a_0}{2ap}\right)^2 = 1 - \frac{a_0}{ap} + \left(\frac{a_0}{2ap}\right)^2 \tag{11.108}$$

15 
$$a = 2\frac{a_0}{p}$$
 (11.109)

Substitution of a given by Eq. (11.109) into Eq. (11.79) gives

$$c' = \frac{a_0}{p} \tag{11.110}$$

The internuclear distance from Eq. (11.110) is

$$2c' = \frac{2a_o}{p} \tag{11.111}$$

Substitution of  $a = \frac{2a_o}{p}$  and  $c' = \frac{a_o}{p}$  into Eq. (11.80) gives the length of the semiminor axis of the prolate spheroidal MO, b = c:

$$b = \frac{\sqrt{3}}{p}a_{\sigma} \tag{11.112}$$

Substitution of  $a = \frac{2a_o}{p}$  and  $c' = \frac{a_o}{p}$  into Eq. (11.67) gives the eccentricity, e:

$$e = \frac{1}{2} \tag{11.113}$$

From Eqs. (11.63-11.65), the result of Eq. (11.113) can be used to the obtain the electric force  $\mathbf{F}_{ele}$  between the protons and the ellipsoidal MO as

$$\mathbf{F}_{ele} = Ze\mathbf{E}\mathbf{i}_{\xi} = h_{2ee}^{-1} \frac{p2e^2}{4\pi\varepsilon_0 ab^2} D\mathbf{i}_{\xi} = \frac{pe^2}{8\pi\varepsilon_0} D\mathbf{i}_{\xi}$$
(11.114)

where the electric field E of the MO is given by Eq. (11.49). Then, the force balance of the hydrogen-type molecular ion is given by

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{p e^2}{8\pi \varepsilon_0} D \tag{11.115}$$

10 which has the parametric solution given by Eq. (11.83) when

$$a = \frac{2a_0}{p} {(11.116)}$$

The solutions for the prolate spheroidal axes and eccentricity are given by Eqs. (11.109-11.113).

#### 15 ENERGIES OF HYDROGEN-TYPE MOLECULAR IONS

From Eq. (11.31), the magnitude of the ellipsoidal field corresponding to a below "ground state" hydrogen-type molecule is an integer, p. The force balance equation (Eq. (11.115)) applies for each point of the electron MO having non-constant charge (mass)-density and velocity over the equipotential and equal energy surface. The electron potential and kinetic 20 energies are thus determined from an ellipsoidal integral.

The potential energy is doubled due to the transverse electric force. The force normal to the MO is given by the dot product of the sum of the force vectors from each focus with  $\hat{\mathbf{d}}$  where the angle  $\beta$  is  $\beta = \frac{\pi}{2} - \alpha$ , and the transverse forces are given by the cross product with  $\hat{\mathbf{d}}$ . As shown in Figure 1, equivalently, the transverse projection is given with the angle 25  $\alpha$  replacing  $\beta$  where the range of  $\alpha$  is the same as  $\beta$ . The two contributions to the

potential energy doubles it. The potential energy,  $V_e$ , of the electron MO in the field of magnitude p times that of the two protons at the foci is

$$V_{e} = 2\frac{-2pe^{2}}{4\pi\varepsilon_{o}}D\frac{ab^{2}}{2D}\int_{\xi}^{\infty}\frac{d\xi}{R_{\xi}}$$

$$= \frac{-4pe^{2}}{8\pi\varepsilon_{o}}\int_{\xi}^{\infty}\frac{d\xi}{(\xi+b)\sqrt{\xi+a}}$$

$$= \frac{-4pe^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}}\ln\frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}$$

$$= \frac{-4pe^{2}}{8\pi\varepsilon_{o}c'}\ln\frac{a+c'}{a-c'}$$
(11.117)

where

$$5 \sqrt{a^2 - b^2} = c' (11.118)$$

2c' is the distance between the foci which is the internuclear distance. The kinetic energy, T, of the electron MO follows from the same type of integral as  $V_e$  using Eqs. (7-14) of Stratton [8], Eqs. (11.37-11.46), and integral #147 of Lide [9]. T is given by the corresponding integral of the centrifugal force (LHS of Eq. (11.115)) with the constraint that the current motion allows the equipotential and equal energy condition with a central field due to the protons; thus, it is corrected by the scale factor  $h_{2cc}$  given by Eq. (11.62). The  $h_{2cc}$  correction can be considered the scaling factor of the moment of inertial such that the kinetic energy is equivalent to the rotational energy for constant angular frequency  $\omega$ . The kinetic energy, T, of the electron MO is given by

15 
$$T = h_{2cc} \frac{-\hbar^2}{m_e a^2 b^2} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}} = \frac{-4\hbar^2}{2m_e a} \int_{\xi}^{\infty} \frac{d\xi}{(\xi + b)\sqrt{\xi + a}} = \frac{-2\hbar^2}{m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(11.119)

The potential energy,  $V_P$ , due to proton-proton repulsion in the field of magnitude p times that of the protons at the foci ( $\xi = 0$ ) is

$$V_{p} = \frac{pe^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}}$$
 (11.120)

20 The total energy,  $E_T$ , is given by the sum of the energy terms

$$E_T = V_e + V_p + T (11.121)$$

Substitution of a and b given by Eqs. (11.109) and (11.112), respectively, into Eqs. (11.117), (11.119), (11.120), and (11.121) gives

$$V_e = \frac{-4p^2e^2}{8\pi\varepsilon_0 a_0} \ln 3 \tag{11.122}$$

$$V_p = \frac{p^2 e^2}{8\pi\varepsilon_0 a_0} \tag{11.123}$$

$$T = \frac{2p^2e^2}{8\pi\varepsilon_0 a_0} \ln 3 \tag{11.124}$$

$$E_r = -13.6 \ eV(4p^2 \ln 3 - p^2 - 2p^2 \ln 3) = -p^2 16.28 \ eV \tag{11.125}$$

5 The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical-mechanics equations of an ellipse that considered only the binding force between the protons and the electron and the electron centrifugal force. T is one-half the magnitude of  $V_e$  as required for an inverse-squared force [1] wherein  $V_e$  is the source of T.

10

#### VIBRATION OF HYDROGEN-TYPE MOLECULAR IONS

A charge, q, oscillating according to  $\mathbf{r}_0(t) = \mathbf{d} \sin \omega_0 t$  has a Fourier spectrum

$$\mathbf{J}(\mathbf{k},\omega) = \frac{q\omega_0 d}{2} J_m(k\cos\theta d) \{\delta[\omega - (m+1)\omega_0] + \delta[\omega - (m-1)\omega_0]\}$$
(11.126)

where  $J_m$ 's are Bessel functions of order m. These Fourier components can, and do, acquire phase velocities that are equal to the velocity of light [10]. The protons of hydrogen-type molecular ions and molecules oscillate as simple harmonic oscillators; thus, vibrating protons will radiate. Moreover, non-oscillating protons may be excited by one or more photons that are resonant with the oscillatory resonance frequency of the molecule or molecular ion, and oscillating protons may be further excited to higher energy vibrational states by resonant photons. The energy of a photon is quantized according to Planck's equation

$$E = \hbar \omega \tag{11.127}$$

The energy of a vibrational transition corresponds to the energy difference between the initial and final vibrational states. Each state has an electromechanical resonance frequency, and the emitted or absorbed photon is resonant with the difference in frequencies. Thus, as a general principle, quantization of the vibrational spectrum is due to the quantized energies of photons and the electromechanical resonance of the vibrationally excited ion or molecule.

It is shown by Fowles [11] that a perturbation of the orbit determined by an inversesquared force results in simple harmonic oscillatory motion of the orbit. In a circular orbit in spherical coordinates, the transverse equation of motion gives

$$\dot{\theta} = \frac{L/m}{r^2} \tag{11.128}$$

5 where L is the angular momentum. The radial equation of motion is

$$m(\ddot{r} - r\dot{\theta}^2) = f(r) \tag{11.129}$$

Substitution of Eq. (11.128) into Eq. (11.129) gives

$$m\ddot{r} - \frac{m(L/m)^2}{r^3} = f(r)$$
 (11.130)

For a circular orbit, r is a constant and  $\ddot{r} = 0$ . Thus, the radial equation of motion is given by

$$10 -\frac{m(L/m)^2}{a^3} = f(a) (11.131)$$

where a is the radius of the circular orbit for central force f(a) at r = a. A perturbation of the radial motion may be expressed in terms of a variable x defined by

$$x = r - a \tag{11.132}$$

The differential equation can then be written as

15 
$$m\ddot{x} - m(L/m)^2(x+a)^{-3} = f(x+a)$$
 (11.133)

Expanding the two terms involving x+a as a power series in x, gives

$$m\ddot{x} - m(L/m)^2 a^{-3} \left(1 - 3\frac{x}{a} + ...\right) = f(a) + f'(a)x + ...$$
 (11.134)

Substitution of Eq. (11.131) into Eq. (11.134) and neglecting terms involving  $x^2$  and higher powers of x gives

20 
$$m\ddot{x} + \left[\frac{-3}{a}f(a) - f'(a)\right]x = 0$$
 (11.135)

For an inverse-squared central field, the coefficient of x in Eq. (11.135) is positive, and the equation is the same as that of the simple harmonic oscillator. In this case, the particle, if perturbed, oscillates harmonically about the circle r = a, and an approximation of the angular frequency of this oscillation is

25 
$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m}} = \sqrt{\frac{k}{m}}$$
 (11.136)

An apsis is a point in an orbit at which the radius vector assumes an extreme value (maximum or minimum). The angle swept out by the radius vector between two consecutive apsides is called the apsidal angle. Thus, the apsidal angle is  $\pi$  for elliptical orbits under the inverse-squared law of force. In the case of a nearly circular orbit, Eq. (11.135) shows that r oscillates about the circle r = a, and the period of oscillation is given by

$$\tau_r = 2\pi \sqrt{\frac{m}{-\left[\frac{3}{a}f(a) + f'(a)\right]}}$$
(11.137)

The apsidal angle in this case is just the amount by which the polar angle  $\theta$  increases during the time that r oscillates from a minimum value to the succeeding maximum value which is  $\tau_r$ . From Eq. (11.128),  $\dot{\theta} = \frac{L/m}{r^2}$ ; therefore,  $\theta$  remains constant, and Eq. (11.131) gives

 $\dot{\theta} \approx \frac{L/m}{a^2} = \left[ -\frac{f(a)}{ma} \right]^{1/2} \tag{11.138}$ 

Thus, the apsidal angle is given by

$$\psi = \frac{1}{2}\tau_{r}\dot{\theta} = \pi \left[ 3 + a \frac{f'(a)}{f(a)} \right]^{-1/2}$$
(11.139)

Thus, the power force of  $f(r) = -cr^n$  gives

$$\psi = \pi \left(3 + n\right)^{-1/2} \tag{11.140}$$

15 The apsidal angle is independent of the size of the orbit in this case. The orbit is re-entrant, or repetitive, in the case of the inverse-squared law (n=-2) for which  $\psi=\pi$ .

A prolate spheroid MO and the definition of axes are shown in Figures 5A and 5B, respectively. Consider the two nuclei A and B, each at focus of the prolate spheroid MO. From Eqs. (11.115), (11.117), and (11.119), the attractive force between the electron and each 20 nucleus at a focus is

$$f(a) = -\frac{pe^2}{4\pi\varepsilon_o a^2} \tag{11.141}$$

and

$$f'(a) = \frac{2pe^2}{4\pi\varepsilon_a a^3} \tag{11.142}$$

In addition to the attractive force between the electron and the nuclei, there is a 25 repulsive force between the two nuclei that is the source of a corresponding reactive force on

the reentrant electron orbit. Consider an elliptical orbital plane cross section of the MO in the xy-plane with a nucleus A at (-c', 0) and a nucleus B at (c', 0). For B acting as the attractive focus, the reactive repulsive force at the point (a, 0), the positive semimajor axis, depends on the distance from (a, 0) to nucleus A at (-c', 0) (i.e. the distance from the position of the electron MO at the semimajor axis to the opposite nuclear repelling center at the opposite focus). The distance is given by the sum of the semimajor axis, a, and c', 1/2 the internuclear distance. The contribution from the repulsive force between the two protons is

$$f(a+c') = \frac{pe^2}{8\pi\varepsilon_o (a+c')^2}$$
 (11.143)

and

10 
$$f'(a+c') = -\frac{pe^2}{4\pi\varepsilon_o (a+c')^3}$$
 (11.144)

Thus, from Eqs. (11.136) and (11.141-11.144), the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{4\pi\varepsilon_o a}{\mu}} \frac{8\pi\varepsilon_o (a+c')}{\mu}$$

$$\sqrt{\frac{pe^2}{4\pi\varepsilon_o \left(\frac{2a_H}{p}\right)^3} - \frac{pe^2}{8\pi\varepsilon_o \left(\frac{3a_H}{p}\right)^3}}$$
(11.145)

 $= p^2 4.44865 \times 10^{14} \ rad/s$ 

where the semimajor axis, a, is  $a = \frac{2a_H}{p}$  according to Eq. (11.116) and c' is  $c' = \frac{a_H}{p}$  according to Eq. (11.110).

In the case of a hydrogen molecule or molecular ion, the electrons which have a mass of 1/1836 that of the protons move essentially instantaneously, and the charge density is that of a continuous membrane. Thus, a stable electron orbit is maintained with oscillatory motion of the protons. Hydrogen molecules and molecular ions are symmetrical along the semimajor axis; thus, the oscillatory motion of protons is along this axis. Let x be the increase in the semimajor due to the reentrant orbit with a corresponding displacement of the protons along the semimajor axis from the position of the initial foci of the stationary state. The equation of proton motion due to the perturbation of an orbit having a central inverse-squared central force [1] and neglecting terms involving  $x^2$  and higher is given by

$$\mu \ddot{\mathbf{x}} + k \mathbf{x} = 0 \tag{11.146}$$

which has the solution in terms of the maximum amplitude of oscillation, A, the reduced nuclear mass,  $\mu$ , the restoring constant or spring constant, k, the resonance angular frequency,  $\omega_0$ , and the vibrational energy,  $E_{vib}$ , [12]

$$5 A\cos\omega_0 t (11.147)$$

where

$$\omega_0 = \sqrt{\frac{k}{\mu}} \tag{11.148}$$

For a symmetrical displacement x, the potential energy corresponding to the oscillation  $E_{Pvib}$  is given by

10 
$$E_{Pvtb} = 2\left(\frac{1}{2}kx^2\right) = kx^2$$
 (11.149)

The total energy of the oscillating molecular ion,  $E_{Totalvib}$ , is given as the sum of the kinetic and potential energies

$$E_{Totalvib} = \frac{1}{2}\mu\dot{x}^2 + kx^2 \tag{11.150}$$

The velocity is zero when x is the maximum amplitude, A. The total energy of the 15 oscillating molecular ion,  $E_{Totalvib}$ , is then given as the potential energy with x = A

$$E_{Totalvib} = kA^2 \tag{11.151}$$

Thus,

$$A = \sqrt{\frac{E_{Totalvib}}{k}} \tag{11.152}$$

It is shown in the Excited States of the One-Electron Atom (Quantization) section that the change in angular frequency of the electron orbitsphere (Eq. (2.21)) is identical to the angular frequency of the photon necessary for the excitation,  $\omega_{photon}$  (Eq. (2.19)). The energy of the photon necessary to excite the equivalent transition in an electron orbitsphere is one-half of the excitation energy of the stationary cavity because the change in kinetic energy of the electron orbitsphere supplies one-half of the necessary energy. The change in the angular frequency of the orbitsphere during a transition and the angular frequency of the photon corresponding to the superposition of the free space photon and the photon corresponding to the kinetic energy change of the orbitsphere during a transition are equivalent. The correspondence principle holds. It can be demonstrated that the resonance condition between

these frequencies is to be satisfied in order to have a net change of the energy field [13]. The bound electrons are excited with the oscillating protons. Thus, the mechanical resonance frequency,  $\omega_0$ , is only one-half that of the electromechanical frequency which is equal to the frequency of the free space photon,  $\omega$ , which excites the vibrational mode of the hydrogen molecular ion. The vibrational energy,  $E_{vib}$ , corresponding to the photon is given by

$$E_{vib} = \hbar \omega = \hbar \omega_0 = \hbar \sqrt{\frac{k}{\mu}} = 2kA^2 \tag{11.153}$$

where Planck's equation (Eq. (11.127)) was used. The reduced mass is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{11.154}$$

10 Thus,

$$A = \sqrt{\frac{\hbar \omega_0}{2k}} \tag{11.155}$$

Since the protons and electron are not fixed, but vibrate about the center of mass, the maximum amplitude is given by the reduced amplitude,  $A_{reduced}$ , given by

$$A_{reduced} = \frac{A_1 A_2}{A_1 + A_2} \tag{11.156}$$

15 where  $A_n$  is the amplitude n if the origin is fixed. Thus, Eq. (11.155) becomes

$$A_{reduced} = \frac{1}{2} \sqrt{\frac{\hbar \omega_0}{2k}} \tag{11.157}$$

and from Eq. (11.148),  $A_{reduced}$  is

$$A_{reduced} = \frac{1}{2} \sqrt{\frac{\hbar \omega_0}{2k}} = \frac{1}{2} \sqrt{\frac{\hbar}{2k}} \left(\frac{k}{\mu}\right)^{1/4} = \frac{\sqrt{\hbar}}{2^{3/2} (k\mu)^{1/4}}$$
(11.158)

Then, from Eq. (11.67),  $A_c$ , the displacement of c' is the eccentricity e given by Eq. 20 (11.113) times  $A_{reduced}$  (Eq. (11.158)):

$$A_{c'} = eA_{reduced} = \frac{A_{reduced}}{2} = \frac{\sqrt{\hbar}}{2^{5/2} (k\mu)^{1/4}}$$
(11.159)

Thus, during bond formation, the perturbation of the orbit determined by an inversesquared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency,  $\omega(0)$ , for a hydrogen-type molecular ion  $H_2^+(1/p)$  given by Eqs. (11.136) and (11.145) is

$$\omega(0) = p^2 \sqrt{\frac{k(0)}{\mu}} = p^2 \sqrt{\frac{165.51 \, Nm^{-1}}{\mu}} = p^2 4.449 \, X \, 10^{14} \, radians / s \tag{11.160}$$

where the reduced nuclear mass of hydrogen given by Eq. (11.154) is

$$5 \mu = 0.5m_a (11.161)$$

and the spring constant, k(0), given by Eqs. (11.136) and (11.145) is

$$k(0) = p^4 165.51 \, Nm^{-1} \tag{11.162}$$

The transition-state vibrational energy,  $E_{vib}(0)$ , is given by Planck's equation (Eq. (11.127)):

$$E_{vib}(0) = \hbar\omega = \hbar p^2 4.44865 \ X \ 10^{14} \ rad / s = p^2 0.2928 \ eV$$
 (11.163)

10 The amplitude of the oscillation,  $A_{reduced}$  (0), given by Eq. (11.158) and Eqs. (11.161-11.162) is

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2} \left(p^4 165.51 \, Nm^{-1} \mu\right)^{1/4}} = \frac{5.952 \, X \, 10^{-12} \, m}{p} = 0.1125 \frac{a_o}{p} \tag{11.164}$$

Then, from Eq. (11.67),  $A_c$ , (0), the displacement of c' is the eccentricity e given by Eq. (11.113) times  $A_{reduced}$  (0) (Eq. (11.164)):

15 
$$A_{c'}(0) = eA_{reduced}(0) = \frac{A_{reduced}(0)}{2} = \frac{\sqrt{\hbar}}{2^{5/2} (k\mu)^{1/4}} = \frac{0.05624a_o}{p}$$
 (11.165)

The spring constant and vibrational frequency for the formed molecular ion are then obtained from Eqs. (11.136) and (11.141-11.145) using the increases in the semimajor axis and internuclear distances due to vibration in the transition state. The vibrational energy,  $E_{vib}(1)$ , for the  $H_2^+(1/p)$   $v=1 \rightarrow v=0$  transition given by adding  $A_{c'}(0)$  (Eq. (11.159)) to the 20 distances a and a+c' in Eqs. (11.145) and (11.163) is

$$E_{vib}(1) = p^2 0.270 \ eV \tag{11.166}$$

where v is the vibrational quantum number.

A harmonic oscillator is a linear system as given by Eq. (11.146). In this case, the predicted resonant vibrational frequencies and energies, spring constants, and amplitudes for 25  $H_2^+(1/p)$  for vibrational transitions to higher energy  $v_i \rightarrow v_f$  are given by  $(v_f - v_i)$  times the corresponding parameters given by Eq. (11.160) and Eqs. (11.162-11.164). However,

excitation of vibration of the molecular ion by external radiation causes the semimajor axis and, consequently, the internuclear distance to increase as a function of the vibrational quantum number v. Consequently, the vibrational energies of hydrogen-type molecular ions are nonlinear as a function of the vibrational quantum number v. The lines become more 5 closely spaced and the change in amplitude,  $\Delta A_{reduced}$ , between successive states becomes larger as higher states are excited due to the distortion of the molecular ion in these states. The energy difference of each successive transition of the vibrational spectrum can be obtained by considering nonlinear terms corresponding to anharmonicity.

The harmonic oscillator potential energy function can be expanded about the 10 internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [14] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods. The energy  $\tilde{v}_v$  of state v is

$$\tilde{v}_{\nu} = \nu \omega_0 - \nu (\nu - 1) \omega_0 x_0, \quad \nu = 0, 1, 2, 3...$$
 (11.167)

15 where

$$\omega_0 x_0 = \frac{hc\omega_0^2}{4D_0} \tag{11.168}$$

 $\omega_0$  is the frequency of the  $\nu=1 \rightarrow \nu=0$  transition corresponding to Eq. (11.166), and  $D_0$  is the bond dissociation energy given by Eq. (11.198). From Eqs. (11.166), (11.168), and (11.198),

$$\omega_0 x_0 = \frac{100hc \left( 8.06573X10^3 \frac{cm^{-1}}{eV} p^2 0.270 eV \right)^2}{4e \left( p^2 2.535 eV + p^3 0.118755 eV \right)} cm^{-1}$$
(11.169)

The vibrational energies of successive states are given by Eqs. (11.166-11.167) and (11.169).

Using Eqs. (11.145), (11.158-11.160), (11.162-11.169), and (11.199) the corresponding parameters for deuterium-type molecular ions with

$$\mu = m_p \tag{11.170}$$

25 are

20

$$\omega(0) = p^2 \sqrt{\frac{k(0)}{\mu}} = p^2 \sqrt{\frac{165.65 \, Nm^{-1}}{\mu}} = p^2 3.147 \, X \, 10^{14} \, radians/s \tag{11.171}$$

$$k(0) = p^4 165.65 Nm^{-1}$$
 (11.172)  
 $E_{vib}(0) = p^2 0.20714 eV$  (11.173)

$$E_{vib}(0) = p^2 0.20714 \ eV \tag{11.173}$$

5

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2} \left(p^4 165.65 \ Nm^{-1}\mu\right)^{1/4}} = \frac{5.004 \ X \ 10^{-12} \ m}{p} = 0.09457 \frac{a_o}{p}$$
(11.174)

$$E_{vib}(1) = p^2 0.193 \ eV \tag{11.175}$$

$$\omega_0 x_0 = \frac{100hc \left( 8.06573X10^3 \frac{cm^{-1}}{eV} p^2 0.193 eV \right)^2}{4e \left( p^2 2.5770 eV + p^3 0.118811 eV \right)} cm^{-1}$$
(11.176)

The vibrational energies of successive states are given by Eqs. (11.167) and (11.175-11.176).

# THE DOPPLER ENERGY TERM OF HYDROGEN-TYPE MOLECULAR IONS

As shown in the Vibration of Hydrogen-type Molecular Ions section, the electron orbiting the nuclei at the foci of an ellipse may be perturbed such that a stable reentrant orbit is established that gives rise to a vibrational state corresponding to time harmonic oscillation of the nuclei and electron. The perturbation is caused by a photon that is resonant with the frequency of oscillation of the nuclei wherein the radiation is electric dipole with the corresponding selection rules.

Oscillation may also occur in the transition state. The perturbation arises from the decrease in internuclear distance as the molecular bond forms. Relative to the unperturbed case given in the Force Balance of Hydrogen-type Molecular Ions section, the reentrant orbit may give rise to a decrease in the total energy while providing a transient kinetic energy to the vibrating nuclei. However, as an additional condition for stability, radiation must be considered. Regarding the potential for radiation, the nuclei may be considered point charges.

20 A point charge undergoing periodic motion accelerates and as a consequence radiates according to the Larmor formula (cgs units) [15]:

$$P = \frac{2e^2}{3c^3} |\dot{\mathbf{v}}|^2 \tag{11.177}$$

where e is the charge,  $\dot{\mathbf{v}}$  is its acceleration, and c is the speed of light. The radiation has a corresponding force that can be determined based on conservation of energy with radiation.

25 The radiation reaction force,  $\mathbf{F}_{rad}$ , given by Jackson [16] is

$$\mathbf{F}_{\rm rad} = \frac{2}{3} \frac{e^2}{c^3} \ddot{\mathbf{v}} \tag{11.178}$$

Then, the Abraham-Lorentz equation of motion is given by [16]

$$m\left(\dot{\mathbf{v}} - \frac{2}{3}\frac{e^2}{mc^3}\ddot{\mathbf{v}}\right) = \mathbf{F}_{\text{ext}} \tag{11.179}$$

where  $\mathbf{F}_{\text{ext}}$  is the external force and m is the mass. The external force for the vibrating system is given by Eq. (11.146).

$$\mathbf{F}_{\text{ext}} = k\mathbf{x} \tag{11.180}$$

5 where x is the displacement of the protons along the semimajor axis from the position of the initial foci of the stationary state in the absence of vibration with a reentrant orbit of the electron. A nonradiative state must be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied.

As shown in the Resonant Line Shape and Lamb Shift section, the spectroscopic linewidth arises from the classical rise-time band-width relationship, and the Lamb Shift is due to conservation of energy and linear momentum and arises from the radiation reaction force between the electron and the photon. The radiation reaction force in the case of the vibration of the molecular ion in the transition state corresponds to a Doppler energy,  $E_D$ , that is dependent on the motion of the electron and the nuclei. The Doppler energy of the electron is given by Eq. (2.146)

$$\overline{E}_D \cong 2\sqrt{E_K E_R} = E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} \tag{11.181}$$

where  $E_R$  is the recoil energy which arises from the photon's linear momentum given by Eq. (2.141),  $E_K$  is the vibrational kinetic energy of the reentrant orbit in the transition state, and M is the mass of the electron  $m_e$ .

As given in the Vibration of Hydrogen-Type Molecular Ions section, for inverse-squared central field, the coefficient of x in Eq. (11.135) is positive, and the equation is the same as that of the simple harmonic oscillator. Since the electron of the hydrogen molecular ion is perturbed as the internuclear separation decreases with bond formation, it oscillates harmonically about the semimajor axis given by Eq. (11.116), and an approximation of the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}}$$
(11.182)

From Eqs. (11.115), (11.117), and (11.119), the central force terms between the electron MO and the two protons are

$$f(a) = -\frac{2pe^2}{4\pi\varepsilon_o a^2} \tag{11.183}$$

and

5

$$f'(a) = \frac{4pe^2}{4\pi\varepsilon_0 a^3} \tag{11.184}$$

Thus, the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\frac{2pe^2}{4\pi\varepsilon_o \left(\frac{2a_H}{p}\right)^3}}{\frac{2a_H}{m_e}}} = p^2 2.06538 \, X \, 10^{16} \, rad/s \tag{11.185}$$

where the semimajor axis, a, is  $a = \frac{2a_H}{p}$  according to Eq. (11.116) including the reduced electron mass. The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar p^2 2.06538 \, X \, 10^{16} \, rad \, / \, s = p^2 13.594697 \, eV$$
 (11.186)

In Eq. (11.181), substitution of the total energy of the hydrogen molecular ion,  $E_T$ , (Eq. 10 (11.125)) for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (11.186) for  $\overline{E}_K$  gives the Doppler energy of the electron for the reentrant orbit.

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -p^2 16.28034 \ eV \sqrt{\frac{2e(p^2 13.594697 \ eV)}{m_e c^2}} = -p^3 0.118755 \ eV$$
(11.187)

The total energy of the molecular ion is decreased by  $\overline{E}_D$ .

In addition to the electron, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency given in the Vibration of Hydrogen-Type Molecular Ions section. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [17]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons,  $\overline{E}_{Kvib}$ , is 1/2 of the vibrational energy of the molecular ion given by Eq. (11.166). The decrease in the energy of the hydrogen molecular ion due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electron and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  and  $\overline{E}_{Kvib}$ . Using Eq. (11.187) and  $E_{vib}$  from Eq. (11.166) gives

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar p^2 \sqrt{\frac{k}{\mu}}$$
(11.188)

$$\overline{E}_{osc} = -p^3 0.118755 \ eV + \frac{1}{2} p^2 (0.29282 \ eV)$$
 (11.189)

To the extent that the MO dimensions are the same, the electron reentrant orbital energies  $\overline{E}_K$  are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies. Using Eq. (11.187) with the deuterium reduced electron mass for  $E_T$  and  $\overline{E}_D$ , and  $E_{vib}$  for  $D_2^+$  (1/p) given by Eq. (11.173), that corresponds to the deuterium reduced nuclear mass (Eq. (11.170)), the corresponding  $\overline{E}_{osc}$  is

$$\overline{E}_{osc} = -p^3 0.118811 \, eV + \frac{1}{2} \, p^2 \left( 0.20714 \, eV \right) \tag{11.190}$$

10

## TOTAL, IONIZATION, AND BOND ENERGIES OF HYDROGEN AND DEUTERIUM MOLECULAR IONS

The total energy of the hydrogen molecular ion which is equivalent to the negative of the ionization energy is given by the sum of  $E_T$  (Eqs. (11.121) and (11.125)) and  $\overline{E}_{osc}$  given by 15 Eqs. (11.185-11.188). Thus, the total energy of the hydrogen molecular ion having a central field of +pe at each focus of the prolate spheroid molecular orbital including the Doppler term is

$$E_T = V_e + V_p + T + \overline{E}_{asc} . \tag{11.191}$$

 $E_{T} = -p^{2} \left\{ \frac{e^{2}}{8\pi\varepsilon_{o}a_{H}} (4\ln 3 - 1 - 2\ln 3) \left[ 1 + p \sqrt{\frac{2\hbar\sqrt{\frac{2e^{2}}{4\pi\varepsilon_{o}(2a_{H})^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\}$   $= -p^{2}16.2803 \ eV - p^{3}0.118811 \ eV + \frac{1}{2} p^{2}\hbar\sqrt{\frac{k}{\mu}}$ (11.192)

From Eqs. (11.189) and (11.191-11.192), the total energy for hydrogen-type molecular ions is

52

$$E_{T} = -p^{2}16.28033 \ eV + \overline{E}_{osc}$$

$$= -p^{2}16.28033 \ eV - p^{3}0.118755 \ eV + \frac{1}{2} p^{2} (0.29282 \ eV)$$

$$= -p^{2}16.13392 \ eV - p^{3}0.118755 \ eV$$
(11.193)

The total energy of the deuterium molecular ion is given by the sum of  $E_r$  (Eq. (11.125)) corrected for the reduced electron mass of D and  $\overline{E}_{osc}$  given by Eq. (11.190):

$$E_{T} = -p^{2}16.284 \ eV + \overline{E}_{osc}$$

$$= -p^{2}16.284 \ eV - p^{3}0.118811 \ eV + \frac{1}{2} p^{2} (0.20714 \ eV)$$

$$= -p^{2}16.180 \ eV - p^{3}0.118811 \ eV$$
(11.194)

5 The bond dissociation energy,  $E_D$ , is the difference between the total energy of the corresponding hydrogen atom or H(1/p) atom [18-19], called hydrino atom having a principal quantum number 1/p where p is an integer, and  $E_T$ .

$$E_D = E(H(1/p)) - E_T \tag{11.195}$$

where [18]

10 
$$E(H(1/p)) = -p^2 13.59844 \ eV$$
 (11.196)

and [19]

$$E(D(1/p)) = -p^2 13.603 \ eV$$
 (11.197)

The hydrogen molecular ion bond energy,  $E_D$ , is given by Eq. (11.193) with the reduced electron mass and Eqs. (11.195-11.196):

$$E_D = -p^2 13.59844 - E_T$$

$$= -p^2 13.59844 - \left(-p^2 16.13392 \ eV - p^3 0.118755 \ eV\right)$$

$$= p^2 2.535 \ eV + p^3 0.118755 \ eV$$
(11.198)

The deuterium molecular ion bond energy,  $E_D$ , is given by Eq. (11.194) with the reduced electron mass of D and Eqs. (11.195) and (11.197):

$$E_D = -p^2 13.603 - E_T$$

$$= -p^2 13.603 - \left(-p^2 16.180 \ eV - p^3 0.118811 \ eV\right)$$

$$= p^2 2.5770 \ eV + p^3 0.118811 \ eV$$
(11.199)

#### 20 HYDROGEN-TYPE MOLECULES

### FORCE BALANCE OF HYDROGEN-TYPE MOLECULES

Hydrogen-type molecules comprise two indistinguishable electrons bound by an elliptic field. Each electron experiences a centrifugal force, and the balancing centripetal force (on each electron) is produced by the electric force between the electron and the elliptic electric field 5 and the magnetic force between the two electrons causing the electrons to pair. In addition to nonradiation, the angular frequency given by Eq. (11.24) corresponds to a Lorentzian invariant magnetic moment of a Bohr magneton,  $\mu_B$ , as given in the Magnetic Moment of an Ellipsoidal MO section. The internal field is uniform along the major axis, and the far field is that of a dipole as shown in the Magnetic Field of an Ellipsoidal MO section. The magnetic 10 force is derived by first determining the interaction of the two electrons due to the field of the outer electron 2 acting on the magnetic moments of electron 1 and vice versa. Insight to the behavior is given by considering the physics of a single bound electron in an externally applied uniform magnetic field as discussed in the Two-Electron Atoms section. The orbitsphere-cvf and the uniform current- (charge-) density function  $Y_0^0\left(\theta,\phi\right)$  was given in the 15 Orbitsphere Equation of Motion for  $\ell = 0$  section and Appendix III. The resultant angular momentum projections of the spherically-symmetric orbitsphere current density,  $Y_0^0(\theta,\phi)$ , are  $L_{xy} = \frac{\hbar}{4}$  and  $L_z = \frac{\hbar}{2}$ . As shown in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section, the electron spin angular momentum gives rise to a trapped photon with h of angular momentum along an S-axis. 20 Then, the spin state of an orbitsphere comprises a photon standing wave that is phasematched to a spherical harmonic source current, a spherical harmonic dipole  $Y_t^m(\theta,\phi) = \sin\theta$ with respect to the S-axis. The dipole spins about the S-axis at the angular velocity given by Eq. (1.55) with h of angular momentum. S rotates about the z-axis at the Larmor frequency at  $\theta = \frac{\pi}{3}$  such that it has a static projection of the angular momentum of 25  $S_{\parallel} = \pm \hbar \cos \frac{\pi}{3} = \pm \frac{\hbar}{2} i_{Z_R}$  as given by Eq. (1.85), and from Eq. (1.84), the projection of S onto the transverse plane (xy-plane) is  $S_{\perp} = \hbar \sin \frac{\pi}{3} = \pm \sqrt{\frac{3}{4}} \hbar i_{\gamma_R}$ . Then, the vector projection of the

radiation-reaction-type magnetic force of the Two Electron Atom section given by Eqs. (7.24)

and (7.31) contain the factor  $\sqrt{\frac{3}{4}}\hbar$ . This represents the maximum projection of the time-dependent magnetic moment onto an axis of the spherical-central-force system.

The orbitsphere can serve as a basis element to form a molecular orbital (MO). The total magnitude of the angular momentum of  $\hbar$  is conserved for each member of the linear 5 combinations of  $Y_0^0(\theta,\phi)$ 's in the transition from the  $Y_0^0(\theta,\phi)$ 's to the MO. Since the charge and current densities are equivalent by the ratio of the frequency, the solution of Laplace's equation for the charge density that is an equipotential energy surface also determines the current density. The frequency and the velocity are given by Newton's laws. Specifically, the further constraint from Newton's laws that the orbital surface is a constant total energy surface 10 and the condition of nonradiation provide that the angular velocity of each point on the surface is constant, the current is continuous and constant, and determines the corresponding velocity function. In non-spherical coordinates, the nonuniform charge distribution given by Laplace's equation is compensated by a nonuniform velocity distribution such that the constant current condition is met. Then, the conservation of the angular momentum is 15 provided by symmetrically stretching the current density along an axis perpendicular to the plane defined by the orthogonal components of angular momentum. The angular momentum projection may be determined by first considering the case of the hydrogen molecular ion. Specifically, the angular momentum must give the results of the Stern-Gerlach experiment as shown for atomic electrons and free electrons in the Resonant Precession of the Spin-1/2-20 Current-Density Function Gives Rise to the Bohr Magneton section and Stern-Gerlach Experiment section, respectively.

The hydrogen-molecular-ion MO, and all MOs in general, have cylindrical symmetry along the bond axis. Thus, for the hydrogen molecular ion, the two orthogonal semiminor axes are equivalent and interchangeable. Then, in general,  $Y_0^0(\theta,\phi)$  can serve as a basis element for an MO having equal angular momentum projections along each of the semiminor axes. This defines the plane and the orthogonal axis for stretching the  $Y_0^0(\theta,\phi)$  basis element to form the MO. Thus, to conserve angular momentum,  $Y_0^0(\theta,\phi)$  is stretched along the semimajor axis as shown in Figure 2. This gives rise to an ellipsoidal surface comprised of the equivalent of elliptical-orbit, plane cross sections in the direction parallel to the semimajor axis with equal angular momentum projections along the orthogonal semiminor axes when the basis element has equal orthogonal angular momentum components.

As shown in the Exact Generation of  $Y_0^0(\theta,\phi)$  from the Orbitsphere-cvf section, the orbitsphere is comprised of the uniform function  $Y_0^0(\theta,\phi)$  corresponding to STEP ONE having the angular momentum components  $\mathbf{L}_{xy}=0$  and  $\mathbf{L}_z=\frac{\hbar}{4}$  and the uniform function  $Y_0^0(\theta,\phi)$  corresponding to STEP TWO having the angular momentum components  $\mathbf{L}_{xy}=\frac{\hbar}{4}$  5 and  $\mathbf{L}_z=\frac{\hbar}{4}$ . These components are separable. Then, the basis element  $Y_0^0(\theta,\phi)$  for the construction of an MO that conserves the total magnitude of the angular momentum of  $\hbar$  (Eq. (1.57)) that matches the MO conditions of equal orthogonal components of angular momentum along each semiminor axis is a single  $Y_0^0(\theta,\phi)$  that is generated according to STEP TWO but with twice the angular momentum in each great-circle basis element to give  $\mathbf{L}_{xy}=\frac{\hbar}{2}$  and  $\mathbf{L}_z=\frac{\hbar}{2}$ .

Now consider the behavior of the hydrogen molecular ion in a magnetic field. As shown in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section, the photon angular momentum corresponding to the resonant excitation of the Larmor excited state is  $\hbar$ , and the angular momentum change corresponding to the spin-flip transition is also  $\hbar$ . Furthermore, torque balance for the orbitsphere was determined by considering the energy minimum due to the interaction of the magnetic moments corresponding to the components of angular momentum. In the case of the hydrogen molecular ion, the Larmor-excitation photon carries  $\hbar$  of angular momentum that gives rise to a prolate spheroidal dipole current about an S-axis in the same manner as in the case of the spherical dipole of the Larmor excited orbitsphere shown in Figures 1.15 and 1.16 in Chapter 1. The former are given by the prolate angular function, which comprises an associated Legendre function  $P_\ell^m(\eta)$  [20], and the latter comprises the spherical harmonic dipole  $Y_\ell^m(\theta,\phi) = \sin\theta$ . Both are with respect to the S-axis. For hydrogen molecular ion,  $\frac{\hbar}{2}$  of intrinsic spin is along each of the semiminor axes of the prolate spheroidal MO. Torque

25 balance is achieved with S along the semimajor axis as shown in Figure 3. Thus, the Larmor excitation is along the semimajor axis. In general, all bonds are cylindrically symmetrical about the internuclear or semimajor axis; thus, the Larmor precession occurs about the bond

axis of an MO wherein the intrinsic angular momentum components rotate about S at the Larmor frequency.

In the coordinate system rotating at the Larmor frequency (denoted by the axes labeled  $X_R$ ,  $Y_R$ , and  $Z_R$  in Figure 2), the angular momentum of S of magnitude  $\hbar$  is stationary. The 5  $Y_R$ -component of magnitude  $\frac{\hbar}{2}$  and the  $Z_R$ -component of magnitude  $\frac{\hbar}{2}$  rotate about S at the Larmor frequency. The rotation occurs due to a resonant excitation that results in a balance between the magnetic moment of S of  $\mu_B$  corresponding to its angular momentum of  $\hbar$  (Eq. (28) of Box 1.3 and Eq. (2.65)) and those of the orthogonal  $\frac{\hbar}{2}$  angular momentum components along  $Z_R$  and  $Y_R$  of  $\frac{\mu_R}{2}$ .

Then, the S-axis is the direction of the magnetic moment of each unpaired electron of a molecule or molecular ion. The magnetic moment of S of  $\mu_B$  corresponding to its  $\hbar$  of angular momentum is consistent with the Stern-Gerlach experiment wherein the Larmor excitation can only be parallel or antiparallel to the magnetic field in order to conserve the angular momentum of the electron, the photon corresponding to the Larmor excitation, and 15 the  $\hbar$  of angular momentum of the photon that causes a 180° flip of the direction of S. The result is the same as that for the atomic electron and the free electron given in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section and Stern-Gerlach Experiment section, respectively. The magnetic field is given in the Magnetic Field of an Ellipsoidal Molecular Orbital section.

20

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Next, consider the magnetic-pairing force of the hydrogen molecule due to the spinangular-momentum components. The magnetic moments of electrons 1 and 2 of the hydrogen molecule cancel as they are spin paired to form an energy minimum at the radius (i.e.  $r_1 = r_2$ ). The magnetic force follows the derivation for that between the electrons of two-25 electron atoms as given in the Two-Electron Atoms section. The latter force was derived by first determining the interaction of the two electrons due to the field of the outer electron 2 acting on the magnetic moments of electron 1 and vice versa. It was also given by the relationship between the angular momentum, energy, and frequency for the transition of electron 2 from the continuum to the ground state. The magnitude of the magnetic force 30 given by Eqs. (7.24) and (7.31) is equivalent to that of the centrifugal force given by Eqs.

(7.1-7.2) multiplied by  $\frac{1}{Z\hbar}$  times the magnitude of the photon angular momentum vector that precesses at the Larmor frequency given by Eq. (7.4). In the present case of hydrogen-type molecules, the radiation-reaction-type magnetic force arises between the electrons, each having the components shown in Figure 3. With the photon angular momentum projection of  $\hbar$  and the total nuclear (non-photon-field) of 2, the magnitude of the magnetic force between the two electrons is 1/2 that of the centrifugal force given by Eq. (11.95).

The hydrogen-type molecule is formed by the binding of an electron 2 to the hydrogen-type molecular ion comprising two protons at the foci of the prolate spheroidal MO of electron 1. The ellipsoids of electron 1 and electron 2 are confocal; thus, the electric fields and the corresponding forces are normal to the each MO of electron 1 and electron 2. The two electrons are bound by the central field of the two protons as in the case of the molecular ion. Since the field of the protons is only ellipsoidal on average, the field of the hydrogen-type molecular ion is not equivalent to an ellipsoid of charge +1 outside of the electron MO. In addition there is a spin pairing force between the two electrons. Due to the force between the centrifugal force and the central field of electron 2 of the protons, the balance between the centrifugal force and the central field of electron 2 of the hydrogen-type molecule formed by electron 2 binding to a hydrogen-type molecular ion also given by Eq. (11.115). The force balance between the centrifugal force and the sum of the Coulombic and magnetic spin-pairing forces to solve for the semimajor axis is

20

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{p e^2}{8\pi \varepsilon_o a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{11.200}$$

$$\frac{2a_o}{pa} - \frac{a_o}{pa} = 1 \tag{11.201}$$

$$a = \frac{a_o}{p} \tag{11.202}$$

Substitution of Eq. (11.202) into Eq. (11.79) is

25 c'

$$c' = \frac{1}{p\sqrt{2}}a_o \tag{11.203}$$

The internuclear distance given by multiplying Eq. (11.203) by two is

$$2c' = \frac{a_o\sqrt{2}}{p} \tag{11.204}$$

Substitution of Eqs. (11.202-11.203) into Eq. (11.80) is

$$b = c = \frac{1}{p\sqrt{2}}a_o \tag{11.205}$$

Substitution of Eqs. (11.202-11.203) into Eq. (11.67) is

$$e = \frac{1}{\sqrt{2}} \tag{11.206}$$

For hydrogen, r(t) = D for  $\theta = n\frac{\pi}{2}$ , n = 0,1,2,3,4. Thus, there is no dipole moment and the

5 molecule is not predicted to be infrared active. However, it is predicted to be Raman active due to the quadrupole moment. The liquefaction temperature of  $H_2$  is also predicted to be significantly higher than isoelectronic helium.

#### **ENERGIES OF HYDROGEN-TYPE MOLECULES**

- 10 The energy components defined previously for the molecular ion, Eqs. (11.117), (11.119), (11.120), and (11.121), apply in the case of the corresponding molecule except that all of the field lines of the protons must end on the MO comprising two-paired electrons. With spin pairing of the mirror-image-current electrons, the scaling factors due to the non-ellipsoidal variation of the electric field of the protons is unity as in the case of the sum of squares of spherical harmonics. Thus, the hydrogen-type molecular energies are given by the integral of the forces without correction. Then, each molecular-energy component is given by the integral of corresponding force in Eq. (11.200) where each energy component is the total for the two equivalent electrons with the central-force action at the position of the electron MO where the parameters a and b are given by Eqs. (11.202) and (11.205), respectively.
- The potential energy,  $V_e$ , of the two-electron MO comprising equivalent electrons in the field of magnitude p times that of the two protons at the foci is

$$V_{\epsilon} = 2\frac{-pe^2}{4\pi\varepsilon_o} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}}$$

$$= \frac{-2pe^2}{8\pi\varepsilon_o} \int_{\xi}^{\infty} \frac{d\xi}{(\xi+b)\sqrt{\xi+a}}$$

$$= \frac{-2pe^2}{8\pi\varepsilon_o \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}$$
(11.207)

which is equivalent to Ze = 2pe times the potential of the MO given by Eq. (11.46) after Eq. (11.114). The potential energy,  $V_p$ , due to proton-proton repulsion in the field of magnitude p times that of the protons at the foci ( $\xi = 0$ ) is

$$V_{p} = \frac{p}{8\pi\varepsilon_{0}} \frac{e^{2}}{\sqrt{a^{2} - b^{2}}}$$
 (11.208)

The kinetic energy, T, of the two-electron MO of total mass  $2m_e$  is

$$T = 2 \frac{-\hbar^2}{2m_e a^2 b^2} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}}$$

$$= \frac{-\hbar^2}{2m_e a} \int_{\xi}^{\infty} \frac{d\xi}{(\xi + b)\sqrt{\xi + a}}$$

$$= \frac{\hbar^2}{2m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(11.209)

The magnetic energy,  $V_m$ , of the two-electron MO of total mass  $2m_e$  corresponding to the 5 magnetic force of Eq. (11.200) is

$$V_{m} = 2 \frac{-\hbar^{2}}{2(2m_{e})a^{2}b^{2}} D \frac{ab^{2}}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_{\xi}}$$

$$= \frac{-\hbar^{2}}{4m_{e}a} \int_{\xi}^{\infty} \frac{d\xi}{(\xi+b)\sqrt{\xi+a}}$$

$$= \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}$$
(11.210)

The total energy,  $E_T$ , is given by the sum of the energy terms (Eqs. (11.207-11.210)):

$$E_T = V_e + T + V_m + V_n \tag{11.211}$$

$$E_T = -13.60 \ eV \left[ \left( 2p^2 \sqrt{2} - p^2 \sqrt{2} + \frac{p^2 \sqrt{2}}{2} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - p^2 \sqrt{2} \right] = -p^2 31.63 \quad (11.212)$$

where a and b are given by Eqs. (11.202) and (11.205), respectively. The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical mechanics equation of an ellipse that considered only the binding force between the protons and the electrons and the electron centrifugal force. As shown by Eqs. (11.290) and (11.292), T is one-half the magnitude of  $V_e$  as required for an inverse-squared force [1] wherein  $V_e$  is the source of T.

#### VIBRATION OF HYDROGEN-TYPE MOLECULES

The vibrational energy levels of hydrogen-type molecules may be solved in the same manner as hydrogen-type molecular ions given in the Vibration of Hydrogen-type Molecular Ions 20 section. The corresponding central force terms of Eq. (11.136) are

$$f(a) = -\frac{pe^2}{8\pi\varepsilon_0 a^2} \tag{11.213}$$

and

$$f'(a) = \frac{pe^2}{4\pi\varepsilon_0 a^3} \tag{11.214}$$

The distance for the reactive nuclear-repulsive terms is given by the sum of the semimajor a, a, and c', 1/2 the internuclear distance. The contribution from the repulsive force between the two protons is

$$f(a+c') = \frac{pe^2}{8\pi\varepsilon_o(a+c')^2} \tag{11.215}$$

and

$$f'(a+c') = -\frac{pe^2}{4\pi\varepsilon_o (a+c')^3}$$
 (11.216)

10 Thus, from Eqs. (11.136) and (11.213-11.216), the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{\frac{pe^2}{8\pi\varepsilon_o a^3} \frac{pe^2}{8\pi\varepsilon_o (a+c')^3}}{\mu}} = \sqrt{\frac{\frac{pe^2}{8\pi\varepsilon_o \left(\frac{a_0}{p}\right)^3}}{\frac{8\pi\varepsilon_o \left(\frac{1+\frac{1}{\sqrt{2}}\right)a_0}{p}\right)^3}{\mu}}} = p^2 8.62385 \times 10^{14} \ rad/s$$
(11.217)

where the semimajor axis, a, is  $a = \frac{a_0}{p}$  according to Eq. (11.202) and c' is  $c' = \frac{a_0}{p\sqrt{2}}$ 

according to Eq. (11.203). Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency,  $\omega(0)$ , for a hydrogen-type molecule  $H_2(1/p)$  given by Eqs. (11.136) and (11.145) is

$$\omega(0) = p^2 \sqrt{\frac{k(0)}{\mu}} = p^2 \sqrt{\frac{621.98 \ Nm^{-1}}{\mu}} = p^2 8.62385 \ X \ 10^{14} \ radians / s$$
 (11.218)

where the reduced nuclear mass of hydrogen is given by Eq. (11.161) and the spring constant, k(0), given by Eqs. (11.136) and (11.217) is

$$k(0) = p^4 621.98 Nm^{-1}$$
 (11.219)

The transition-state vibrational energy,  $E_{vib}(0)$ , is given by Planck's equation (Eq. (11.127)):

$$E_{vib}(0) = \hbar\omega = \hbar p^2 8.62385 X 10^{14} rad/s = p^2 0.56764 eV$$
 (11.220)

The amplitude of oscillation,  $A_{reduced}(0)$ , given by Eqs. (11.158), (11.161), and (11.219) is

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2} \left(p^4 621.98 \ Nm^{-1}\mu\right)^{1/4}} = \frac{4.275 \ X \ 10^{-12} \ m}{p} = 0.08079 \frac{a_o}{p}$$
(11.221)

Then, from Eq. (11.67),  $A_{c'}(0)$ , the displacement of c' is the eccentricity e given by Eq. 5 (11.206) times  $A_{reduced}(0)$  (Eq. (11.221)):

$$A_{c'}(0) = eA_{reduced}(0) = \frac{A_{reduced}(0)}{\sqrt{2}} = \frac{\sqrt{h}}{4(k\mu)^{1/4}} = \frac{0.05713a_o}{p}$$
(11.222)

The spring constant and vibrational frequency for the formed molecule are then obtained from Eqs. (11.136) and (11.213-11.222) using the increases in the semimajor axis and internuclear distances due to vibration in the transition state. The vibrational energy,  $E_{vib}(1)$ , for the  $H_2(1/p)$   $v=1 \rightarrow v=0$  transition given by adding  $A_c(0)$  (Eq. (11.222)) to the distances a and a+c' in Eqs. (11.213-11.220) is

$$E_{vth}(1) = p^2 0.517 \ eV \tag{11.223}$$

where v is the vibrational quantum number. Using Eq. (11.176) with Eqs. (11.223) and (11.252), the anharmonic perturbation term,  $\omega_0 x_0$ , of  $H_2(1/p)$  is

$$\omega_0 x_0 = \frac{100hc \left( 8.06573X10^3 \frac{cm^{-1}}{eV} p^2 0.517 eV \right)^2}{4e \left( p^2 4.151 eV + p^3 0.326469 eV \right)} cm^{-1}$$
(11.224)

where  $\omega_0$  is the frequency of the  $\upsilon=1\rightarrow\upsilon=0$  transition corresponding to Eq. (11.223) and  $D_0$  is the bond dissociation energy given by Eq. (11.252). The vibrational energies of successive states are given by Eqs. (11.167) and (11.223-11.224).

Using the reduced nuclear mass given by Eq. (11.170), the corresponding parameters 20 for deuterium-type molecules  $D_2(1/p)$  (Eqs. (11.213-11.224) and (11.253)) are

$$\omega(0) = p^2 \sqrt{\frac{k(0)}{\mu}} = p^2 \sqrt{\frac{621.98 \, Nm^{-1}}{\mu}} = p^2 6.09798 \, X \, 10^{14} \, radians / s \tag{11.225}$$

$$k(0) = p^4 621.98 Nm^{-1}$$
 (11.226)

$$E_{vib}(0) = p^2 0.4014 \ eV \tag{11.227}$$

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$$A_{reduced}\left(0\right) = \frac{\sqrt{\hbar}}{2^{3/2} \left(p^4 621.98 \ Nm^{-1}\mu\right)^{1/4}} = \frac{3.595 \ X \ 10^{-12} \ m}{p} = 0.06794 \frac{a_o}{p}$$
(11.228)

$$E_{vib}(1) = p^2 0.371 \, eV \tag{11.229}$$

$$\omega_0 x_0 = \frac{100hc \left( 8.06573X10^3 \frac{cm^{-1}}{eV} p^2 0.371 eV \right)^2}{4e \left( p^2 4.229 eV + p^3 0.326469 eV \right)} cm^{-1}$$
(11.230)

The vibrational energies of successive states are given by Eqs. (11.167) and (11.229-11.230).

### THE DOPPLER ENERGY TERM OF HYDROGEN-TYPE MOLECULES

The radiation reaction force in the case of the vibration of the molecule in the transition state also corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. Here, a nonradiative state must also be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. Typically, a third body is required to form hydrogen-type molecules. For example, the exothermic chemical reaction of H+H to form  $H_2$  does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body, M, to remove the bond energy— $H+H+M \rightarrow H_2+M^*$  [21]. The third body distributes the energy from the exothermic reaction, and the end result is the  $H_2$  molecule and an increase in the temperature of the system. Thus, a third body removes the energy corresponding to the additional force term given by Eq. (11.180). From Eqs. (11.200), (11.207) and (11.209), the central force terms between the electron MO and the two protons are

$$f(a) = -\frac{pe^2}{4\pi\varepsilon_0 a^2} \tag{11.231}$$

and

5

$$f'(a) = \frac{2pe^2}{4\pi\varepsilon_a a^3} \tag{11.232}$$

Thus, the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\frac{pe^2}{4\pi\varepsilon_o \left(\frac{a_0}{p}\right)^3}}{\frac{a_0}{m_e}}} = p^2 4.13414 \times 10^{16} \ rad/s \tag{11.233}$$

where the semimajor axis, a, is  $a = \frac{a_0}{p}$  according to Eq. (11.202). The kinetic energy,  $E_K$ , is given by Planckle a greation (Fig. (11.103)).

is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar \omega = \hbar p^2 4.13414 \, X \, 10^{16} \, rad/s = p^2 27.2116 \, eV$$
 (11.234)

In Eq. (11.181), substitution of the total energy of the hydrogen molecule,  $E_T$ , (Eq. (11.212))

5 for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (11.234) for  $\overline{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit.

$$\overline{E}_D \cong E_{hv} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.635 p^2 \ eV \sqrt{\frac{2e(p^2 27.216 \ eV)}{m_e c^2}} = -p^3 0.326469 \ eV \qquad (11.235)$$

The total energy of the molecule is decreased by  $\overline{E}_D$ .

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency given in the Vibration of Hydrogen-Type Molecules section. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [17]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons,  $\overline{E}_{Kvib}$ , is 1/2 of the vibrational energy of the molecule given by Eq. (11.148). The decrease in the energy of the hydrogen molecule due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{asc}$ , is given by the sum of the corresponding energies,  $\overline{E}_{D}$  and  $\overline{E}_{Kvib}$ . Using Eq. (11.235) and  $E_{vib}$  from Eq. (11.220) gives

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar p^2 \sqrt{\frac{k}{\mu}}$$
(11.236)

$$\overline{E}_{osc} = -p^3 0.326469 \ eV + \frac{1}{2} p^2 (0.56764 \ eV)$$
 (11.237)

To the extent that the MO dimensions are the same, the electron reentrant orbital energies,  $\overline{E}_K$ , are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies. Using Eq. (11.235) and  $E_{vib}$  for  $D_2(1/p)$  given by Eq. (11.227), that corresponds to the deuterium reduced nuclear mass (Eq. 25 (11.170)), the corresponding  $\overline{E}_{asc}$  is

$$\overline{E}_{osc} = -p^3 \, 0.326469 \, eV + \frac{1}{2} \, p^2 \, (0.401380 \, eV) \tag{11.238}$$

# TOTAL, IONIZATION, AND BOND ENERGIES OF HYDROGEN AND DEUTERIUM MOLECULES

The total energy of the hydrogen molecule is given by the sum of  $E_T$  (Eqs. (11.211-11.212))

5 and  $\overline{E}_{osc}$  given Eqs. (11.233-11.236). Thus, the total energy of the hydrogen molecule having a central field of +pe at each focus of the prolate spheroid molecular orbital including the Doppler term is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$
 (11.239)

$$E_{T} = -p^{2} \left\{ \frac{e^{2}}{8\pi\varepsilon_{o}a_{0}} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - \sqrt{2} \right] \left[ 1 + p \sqrt{\frac{2\hbar\sqrt{\frac{e^{2}}{4\pi\varepsilon_{o}a_{0}^{3}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right]$$

$$= -p^{2}31.635 \ eV - p^{3}0.326469 \ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

$$(11.240)$$

From Eqs. (11.237) and (11.239-11.240), the total energy for hydrogen-type molecules is

$$E_T = -p^2 31.635 \ eV + \overline{E}_{osc}$$

$$= -p^2 31.635 \ eV - p^3 0.326469 \ eV + \frac{1}{2} p^2 (0.56764 \ eV)$$

$$= -p^2 31.351 \ eV - p^3 0.326469 \ eV$$
(11.241)

The total energy of the deuterium molecule is given by the sum of  $E_T$  (Eq. (11.212)) and  $\overline{E}_{osc}$  15 given by Eq. (11.238):

$$E_{T} = -p^{2}31.6354 \ eV + \overline{E}_{osc}$$

$$= -p^{2}31.6354 \ eV - p^{3}0.326469 \ eV + \frac{1}{2}p^{2}(0.401380 \ eV)$$

$$= -p^{2}31.4345 \ eV - p^{3}0.326469 \ eV$$
(11.242)

The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical mechanics equation of an ellipse that considered only the binding force between the protons and the electrons, the spin20 pairing force, and the electron centrifugal force.

The first ionization energy of the hydrogen molecule,  $IP_1$ ,

65

$$H_2(1/p) \to H_2^+(1/p) + e^-$$
 (11.243)

is given by the difference of Eqs. (11.193) and (11.241):

$$IP_1 = E_T (H_2^+(1/p)) - E_T (H_2(1/p))$$

$$= -p^2 16.13392 \ eV - p^3 0.118755 \ eV - (-p^2 31.351 \ eV - p^3 0.326469 \ eV) (11.244)$$

$$= p^2 15.2171 \ eV + p^3 0.207714 \ eV$$

The second ionization energy,  $IP_2$ , is given by the negative of Eq. (11.193).

$$IP_{2} = p^{2}16.13392 \ eV + p^{3}0.118755 \ eV \tag{11.245}$$

The first ionization energy of the deuterium molecule, IP1,

$$D_2(1/p) \to D_2^+(1/p) + e^-$$
 (11.246)

is given by the difference of Eqs. (11.194) and (11.242):

$$IP_1 = E_T (D_2^+ (1/p)) - E_T (D_2 (1/p))$$

$$= -p^2 16.180 \ eV - p^3 0.118811 \ eV - (-p^2 31.4345 \ eV - p^3 0.326469 \ eV) \quad (11.247)$$

$$= p^2 15.255 \ eV + p^3 0.2077 \ eV$$

10 The second ionization energy,  $IP_2$ , is given by the negative of Eq. (11.194).

$$IP_2 = p^2 16.180 \ eV + p^3 0.118811 \ eV$$
 (11.248)

The bond dissociation energy,  $E_{\scriptscriptstyle D}$ , is the difference between the total energy of the corresponding hydrogen atoms and  $E_{\scriptscriptstyle T}$ 

$$E_D = E(2H(1/p)) - E_T \tag{11.249}$$

15 where [18]

$$E(2H(1/p)) = -p^2 27.20 \ eV \tag{11.250}$$

and [19]

$$E(2D(1/p)) = -p^2 27.206 \ eV \tag{11.251}$$

The hydrogen bond energy,  $E_D$ , is given by Eqs. (11.249-11.250) and (11.241):

$$E_D = -p^2 27.20 \ eV - E_T$$

$$= -p^2 27.20 \ eV - \left(-p^2 31.351 \ eV - p^3 0.326469 \ eV\right)$$

$$= p^2 4.151 \ eV + p^3 0.326469 \ eV$$
(11.252)

The deuterium bond energy,  $E_D$ , is given by Eqs. (11.249), (11.251), and (11.242):

$$E_D = -p^2 27.206 \ eV - E_T$$

$$= -p^2 27.206 \ eV - \left(-p^2 31.4345 \ eV - p^3 0.326469 \ eV\right)$$

$$= p^2 4.229 \ eV + p^3 0.326469 \ eV$$
(11.253)

## THE HYDROGEN MOLECULAR ION H<sub>2</sub>[2c' = 2a<sub>o</sub>]<sup>+</sup>

#### 5 FORCE BALANCE OF HYDROGEN MOLECULAR ION

Force balance between the electric and centrifugal forces is given by Eq. (11.115) where p=1

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi \varepsilon_o a b^2} D \tag{11.254}$$

which has the parametric solution given by Eq. (11.83) when

10 
$$a = 2a_o$$
 (11.255)

The semimajor axis, a, is also given by Eq. (11.116) where p=1. The internuclear distance, 2c', which is the distance between the foci is given by Eq. (11.111) where p=1.

$$2c' = 2a_a (11.256)$$

The experimental internuclear distance is  $2a_o$ . The semiminor axis is given by Eq. (11.112) 15 where p=1.

$$b = \sqrt{3}a_a \tag{11.257}$$

The eccentricity, e, is given by Eq. (11.113).

$$e = \frac{1}{2} \tag{11.258}$$

#### 20 ENERGIES OF THE HYDROGEN MOLECULAR ION

The potential energy,  $V_e$ , of the electron MO in the field of the protons at the foci ( $\xi = 0$ ) is given by Eq. (11.117) where p = 1

$$V_{e} = \frac{-4e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}$$
(11.259)

The potential energy,  $V_p$ , due to proton-proton repulsion is given by Eq. (11.120) where p=1

$$V_p = \frac{e^2}{8\pi s_o \sqrt{\alpha^2 - b^2}} \tag{11.260}$$

The kinetic energy, T, of the electron MO is given by Eq. (11.119) where p=1

$$T = \frac{2\hbar^2}{m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(11.261)

Substitution of a and b given by Eqs. (11.255) and (11.257), respectively, into Eqs. (11.259-5 11.261) is

$$V_e = \frac{-4e^2}{8\pi\varepsilon_o a_H} \ln 3 = -59.7575 \ eV \tag{11.262}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_o a_H} = 13.5984 \ eV \tag{11.263}$$

$$T = \frac{2e^2}{8\pi\varepsilon_o a_H} \ln 3 = 29.8787 \ eV \tag{11.264}$$

The Doppler term,  $\overline{E}_{osc}$ , for hydrogen and deuterium are given by Eqs. (11.189) and (11.190), 10 respectively, where p=1

$$\overline{E}_{osc}(H_2^+) = \overline{E}_D + \overline{E}_{Kvib} = -0.118755 \ eV + \frac{1}{2}(0.29282 \ eV) = 0.027655$$
 (11.265)

$$\overline{E}_{osc}(D_2^+) = -0.118811 \ eV + \frac{1}{2}(0.20714 \ eV) = -0.01524 \ eV$$
 (11.266)

The total energy,  $E_T$ , for the hydrogen molecular ion given by Eqs. (11.191-11.193) is

$$E_{T} = -\left\{ \frac{e^{2}}{8\pi e_{o}a_{H}} (4\ln 3 - 1 - 2\ln 3) \left[ 1 + \sqrt{\frac{2e^{2}}{4pe_{o}(2a_{H})^{3}}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{m}} \right\}$$

$$= -16.2803 \ eV - 0.118811 \ eV + \frac{1}{2} (0.29282 \ eV)$$

$$= -16.2527 \ eV$$
(11.267)

where in Eqs. (11.262-11.267), the radius of the hydrogen atom  $a_H$  (Eq. (1.287)) was used in place of  $a_0$  to account for the corresponding electrodynamic force between the electron and the nuclei as given in the case of the hydrogen atom by Eq. (1.231). The negative of Eq. (11.267) is the ionization energy of  $H_2^+$  and the second ionization energy,  $IP_2$ , of  $H_2$ . From

Eqs. (11.191-11.192) and (11.194), the total energy,  $E_T$ , for the deuterium molecular ion (the ionization energy of  $D_2^+$  and the second ionization energy,  $IP_2$ , of  $IP_2$ 0 is

$$E_T = -16.284 \ eV - 0.118811 \ eV + \frac{1}{2} (0.20714 \ eV) = -16.299 \ eV \tag{11.268}$$

The bond dissociation energy,  $E_D$ , is the difference between the total energy of the 5 corresponding hydrogen atom and  $E_T$ . The hydrogen molecular ion bond energy,  $E_D$ , including the reduced electron mass given by Eq. (11.198) where p=1 is

$$E_D = 2.535 \, eV + 0.118755 \, eV = 2.654 \, eV$$
 (11.269)

The experimental bond energy of the hydrogen molecular ion [22] is

$$E_D = 2.651 \, eV \tag{11.270}$$

10 From Eq. (11.199) where p=1, the deuterium molecular ion bond energy,  $E_D$ , including the reduced electron mass of D is

$$E_D = 2.5770 \ eV + 0.118811 \ eV = 2.6958 \ eV$$
 (11.271)

The experimental bond energy of the deuterium molecular ion [23] is

$$E_D = 2.691 \, eV \tag{11.272}$$

15

#### VIBRATION OF THE HYDROGEN MOLECULAR ION

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for  $H_2^+$  given by Eq. (11.160) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{165.51 \, Nm^{-1}}{\mu}} = 4.449 \, X \, 10^{14} \, radians / s \tag{11.273}$$

wherein p=1. The spring constant, k(0), for  $H_2^+$  given by Eq. (11.162) is

$$k(0) = 165.51 \, Nm^{-1}$$
 (11.274)

The vibrational energy,  $E_{vib}(0)$ , of  $H_2^+$  during bond formation given by Eq. (11.163) is

$$E_{vib}(0) = 0.29282 \ eV \tag{11.275}$$

25 The amplitude of oscillation given by Eq. (11.164) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2} \left(165.51 \ Nm^{-1}\mu\right)^{1/4}} = 5.952 \ X \ 10^{-12} \ m = 0.1125 a_o \tag{11.276}$$

The vibrational energy for the  $H_2^+$   $v=1 \rightarrow v=0$  transition given by Eq. (11.166) is

$$E_{vib}(1) = 0.270 \ eV \tag{11.277}$$

The experimental vibrational energy of  $H_2^+$  [14, 19] is

$$E_{vih} = 0.271 \ eV \tag{11.278}$$

5 The anharmonicity term of  $H_2^+$  given by Eq. (11.169) is

$$\omega_0 x_0 = 55.39 \text{ cm}^{-1} \tag{11.279}$$

The experimental anharmonicity term of  $H_2^+$  from NIST [19] is

$$\omega_{o}x_{o} = 66.2 \text{ cm}^{-1} \tag{11.280}$$

The vibrational energy for the  $D_2^+$   $v=1 \rightarrow v=0$  transition given by Eq. (11.175) is

$$E_{vib} = 0.193 \ eV \tag{11.281}$$

The vibrational energy of the  $D_2^{+}$  [19] based on calculations from experimental data is

$$E_{\rm orb} = 0.196 \ eV \tag{11.282}$$

The anharmonicity term of  $D_2^+$  given by Eq. (11.176) is

$$\omega_0 x_0 = 27.86 \ cm^{-1} \tag{11.283}$$

15 The experimental anharmonicity term of  $D_2^+$  for the state  $X^{-2} \sum_{g}^{+1} s\sigma$  is not given, but the

term for state  $B^{-2}\sum_{g}^{+3}d\sigma$  from NIST [19] is

$$\omega_{x} = 2.62 \text{ cm}^{-1} \tag{11.284}$$

## THE HYDROGEN MOLECULE $H_2[2c' = \sqrt{2}a_o]$

20

#### FORCE BALANCE OF THE HYDROGEN MOLECULE

The force balance equation for the hydrogen molecule is given by Eq. (11.200) where p = 1

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_o ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{11.285}$$

which has the parametric solution given by Eq. (11.83) when

$$25 a = a_o (11.286)$$

The semimajor axis, a, is also given by Eq. (11.202) where p=1. The internuclear distance, 2c', which is the distance between the foci is given by Eq. (11.204) where p=1.

70

$$2c' = \sqrt{2}a_o \tag{11.287}$$

The experimental internuclear distance is  $\sqrt{2}a_o$ . The semiminor axis is given by Eq. (11.205) where p=1.

$$b = \frac{1}{\sqrt{2}} a_o \tag{11.288}$$

5 The eccentricity, e, is given by Eq. (11.206).

$$e = \frac{1}{\sqrt{2}} \tag{11.289}$$

The finite dimensions of the hydrogen molecule are evident in the plateau of the resistivity versus pressure curve of metallic hydrogen [24].

#### 10 ENERGIES OF THE HYDROGEN MOLECULE

The energies of the hydrogen molecule are given by Eqs. (11.207-11.210) where p=1

$$V_e = \frac{-2e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -67.8358 \ eV$$
 (11.290)

$$V_p = \frac{e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} = 19.2415 \ eV \tag{11.291}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 33.9179 \ eV$$
 (11.292)

15 The energy,  $V_m$ , of the magnetic force is

$$V_{m} = \frac{-\hbar^{2}}{4m_{c}a\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} = -16.9589 \ eV$$
 (11.293)

The Doppler terms,  $\overline{E}_{osc}$ , for hydrogen and deuterium molecules are given by Eqs. (11.237) and (11.238), respectively, where p=1

$$\overline{E}_{osc}(H_2) = \overline{E}_D + \overline{E}_{Kvib} = -0.326469 \ eV + \frac{1}{2}(0.56764 \ eV) = -0.042649 \ eV$$
 (11.294)

20 
$$\overline{E}_{osc}(D_2) = -0.326469 \ eV + \frac{1}{2}(0.401380 \ eV) = -0.125779 \ eV$$
 (11.295)

The total energy,  $E_T$ , for the hydrogen molecule given by Eqs. (11.239-11.241) is

$$E_{T} = -\begin{cases} e^{2} \\ \frac{e^{2}}{8\pi\varepsilon_{o}a_{0}} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - \sqrt{2} \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{e^{2}}{4\pi\varepsilon_{o}a_{0}^{3}}}}{m_{e}}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{cases}$$

$$= -31.635 \ eV - 0.326469 \ eV + \frac{1}{2} \left( 0.56764 \ eV \right)$$

$$= -31.6776 \ eV$$

$$(11.29)$$

6)

From Eqs. (11.239-11.240) and (11.242), the total energy,  $E_T$ , for the deuterium molecule is

$$E_T = -31.635 \ eV - 0.326469 \ eV + \frac{1}{2} (0.401380 \ eV) = -31.7608 \ eV \tag{11.297}$$

5 The first ionization energies of the hydrogen and deuterium molecules,  $IP_1$ , (Eqs. (11.243) and (11.246)) are given by the differences in the total energy of corresponding molecular ions and molecules which are given by Eqs. (11.244) and (11.247), respectively, where p=1:

$$IP_1(H_2) = 15.2171 \ eV + 0.207714 \ eV = 15.4248 \ eV$$
 (11.298)

$$IP_1(D_2) = 15.255 \ eV + 0.2077 \ eV = 15.4627 \ eV$$
 (11.299)

10 The bond dissociation energy,  $E_D$ , is the difference between the total energy of two of the corresponding hydrogen atoms and  $E_T$ . The hydrogen molecular bond energy,  $E_D$ , given by Eq. (11.252) where p=1 is

$$E_D = 4.151 \ eV + 0.326469 \ eV = 4.478 \ eV \tag{11.300}$$

The experimental bond energy of the hydrogen molecule [22] is

15 
$$E_D = 4.478 \ eV$$
 (11.301)

The deuterium molecular bond energy,  $E_D$ , given by Eq. (11.253) where p=1 is

$$E_D = 4.229 \ eV + 0.326469 \ eV = 4.556 \ eV \tag{11.302}$$

The experimental bond energy of the deuterium molecule [22] is

$$E_D = 4.556 \ eV \tag{11.303}$$

20

#### VIBRATION OF THE HYDROGEN MOLECULE

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for  $H_2$  given by Eq. (11.218) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{621.98 \ Nm^{-1}}{\mu}} = 8.62385 \ X \ 10^{14} \ radians / s$$
 (11.304)

The spring constant, k(0), for  $H_2$  given by Eq. (11.219) is

$$k(0) = 621.98 Nm^{-1}$$
 (11.305)

wherein p=1. The vibrational energy,  $E_{vib}(0)$ , of  $H_2$  during bond formation given by Eq. 5 (11.220) is

$$E_{vib}(0) = 0.56764 \ eV \tag{11.306}$$

The amplitude of oscillation given by Eq. (11.221) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2} \left(p^4 621.98 \ Nm^{-1}\mu\right)^{1/4}} = 4.275 \ X \ 10^{-12} \ m = 0.08079 a_o$$
 (11.307)

The vibrational energy for the  $H_2$   $v=1 \rightarrow v=0$  transition given by Eq. (11.223) is

10 
$$E_{vib}(1) = 0.517 \ eV$$
 (11.308)

The experimental vibrational energy of  $H_2$  [25-26] is

$$E_{vib}(1) = 0.5159 \ eV \tag{11.309}$$

The anharmonicity term of  $H_2$  given by Eq. (11.224) is

$$\omega_0 x_0 = 120.4 \ cm^{-1} \tag{11.310}$$

15 The experimental anharmonicity term of  $H_2$  from Huber and Herzberg [23] is

$$\omega_e x_e = 121.33 \text{ cm}^{-1} \tag{11.311}$$

The vibrational energy for the  $D_2$   $v = 1 \rightarrow v = 0$  transition given by Eq. (11.229) is

$$E_{vib} = 0.371 \, eV \tag{11.312}$$

The experimental vibrational energy of  $D_2$  [14, 19] is

$$E_{vib} = 0.371 \, eV \tag{11.313}$$

The anharmonicity term of  $D_2$  given by Eq. (11.230) is

$$\omega_0 x_0 = 60.93 \ cm^{-1} \tag{11.314}$$

The experimental anharmonicity term of  $D_2$  from NIST [19] is

$$\omega_e x_e = 61.82 \ cm^{-1} \tag{11.315}$$

The results of the determination of the bond, vibrational, total, and ionization energies, and internuclear distances for hydrogen and deuterium molecules and molecular

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ions are given in Table 11.1. The calculated results are based on first principles and given in closed form equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Despite the predictions of standard quantum mechanics that preclude the imaging of a molecule orbital, the full three-dimensional structure of the outer molecular orbital of  $N_2$  has been recently tomographically reconstructed [27]. The charge-density surface observed is similar to that shown in Figure 5 for  $H_2$  which is direct evidence that electrons are not point-particle probability waves that have no form until they are "collapsed to a point" by measurement. Rather they are physical, two-dimensional equipotential charge density surfaces.

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Table 11.1. The calculated and experimental parameters of  $H_2$ ,  $D_2$ ,  $H_2^+$  and  $D_2^+$ .

Parameter	Calculated	Experimental	Eqs.	Ref. for Exp.
H <sub>2</sub> Bond Energy	4.478 eV	4.478 eV	11.300	22
$D_{\!\scriptscriptstyle 2}$ Bond Energy	4.556 eV	4.556 eV	11.302	22
$H_2^+$ Bond Energy	2.654 eV	2.651 eV	11.269	22
$D_2^+$ Bond Energy	2.696 eV	2.691 eV	11.271	23
H <sub>2</sub> Total Energy	31.677 eV	31.675 eV	11.296	22, 28, 18 <sup>a</sup>
$D_{2}$ Total Energy	31.760 eV	31.760 eV	11.297	19, 23 <sup>6</sup>
$H_{\scriptscriptstyle 2}$ Ionization Energy	15.425 eV	15.426 eV	11.298	28
$D_{\!\scriptscriptstyle 2}$ Ionization Energy	15.463 eV	15.466 eV	11.299	23
$H_2^+$ Ionization Energy	16.253 eV	16.250 eV	11.267	22, 18°
$D_2^+$ Ionization Energy	16.299 eV	16.294 eV	11.268	19, 23 <sup>d</sup>
H <sub>2</sub> <sup>+</sup> Magnetic Moment	9.274 X 10 <sup>-24</sup> JT	9.274 X 10 <sup>-24</sup> JT <sup>-1</sup>	13.1-13.7	29
	$\mu_{\scriptscriptstyle B}$	$\mu_{\scriptscriptstyle B}$		
Absolute $H_2$ Gas-	-28.0 ppm	-28.0 ppm	11.411	30-31
Phase				
NMR Shift	0.749.1	0.741 Å	11.287	32
$H_2$ Internuclear	0.748 Å	. 0.741 A	11.201	32
Distance	$\sqrt{2}a_o$			
$D_2$ Internuclear	0.748 Å	0.741 Å	11.287	32
e Distance	$\sqrt{2}a_o$			
$H_2^+$ Internuclear	1.058 Å	1.06 Å	11.256	22
f Distance	$2a_o$			
$D_2^+$ Internuclear	1.058 Å	1.0559 Å	11.256	23
e Distance	$2a_o$	•		
$H_2$ Vibrational Energy	0.517 eV	0.516 eV	11.308	25, 26
$D_2$ Vibrational Energy	0.371 eV	0.371 eV	11.313	14, 19
$H_2 \omega_e x_e$	$120.4 \ cm^{-1}$	121.33 cm <sup>-1</sup>	11.310	23
$D_2 \omega_e x_e$	$60.93 \ cm^{-1}$	$61.82 \ cm^{-1}$	11.314	19
$H_2^+$ Vibrational Energy	0.270 eV	0.271 eV	11.277	14, 19

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		75		
$D_2^+$ Vibrational Energy	0.193 eV	0.196 eV	11.281	19
$H_2$ J=1 to J=0	0.0148 eV	0.01509 eV	13.45	22
Rotational Energy				
$D_2$ J=1 to J=0	0.00741 eV	0.00755 eV	13.37-13.45	22
Rotational Energy				
$H_2^+$ J=1 to J=0	0.00740 eV	0.00739 eV	13.49	22
Rotational Energy				
$D_2^+$ J=1 to J=0	0.00370 eV	0.003723 eV	13.37-13.43,	23
e			13.49	
Rotational Energy				

<sup>&</sup>lt;sup>a</sup> The experimental total energy of the hydrogen molecule is given by adding the first (15.42593 eV) [28] and second (16.2494 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the hydrogen atom (12.59844 eV) [18] and the bond energy of  $H_2^+$  (2.651 eV) [22].

### THE DIHYDRINO MOLECULAR ION $H_2[2c'=a_0]^{\dagger}$

15

#### FORCE BALANCE OF THE DIHYDRINO MOLECULAR ION

Force balance between the electric and centrifugal forces of  $H_2^+(1/2)$  is given by Eq. (11.115) where p=2

$$\frac{\hbar^2}{m_0 a^2 b^2} D = \frac{2pe^2}{8\pi \epsilon_0 ab^2} D \tag{11.316}$$

20 which has the parametric solution given by Eq. (11.83) when

b The experimental total energy of the deuterium molecule is given by adding the first (15.466 eV) [23] and 5 second (16.294 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the deuterium atom (12.603 eV) [19] and the bond energy of  $D_2^+$  (2.692 eV) [23].

<sup>&</sup>lt;sup>c</sup> The experimental second ionization energy of the hydrogen molecule,  $IP_2$ , is given by the sum of the ionization energy of the hydrogen atom (12.59844 eV) [18] and the bond energy of  $H_2^+$  (2.651 eV) [22].

The experimental second ionization energy of the deuterium molecule,  $IP_2$ , is given by the sum of the lonization energy of the deuterium atom (12.603 eV) [19] and the bond energy of  $D_2^+$  (2.692 eV) [23].

 $<sup>^{</sup>m e}$  The internuclear distances are not corrected for the reduction due to  $\overline{E}_{
m asc}$  .

 $<sup>^{</sup> ext{f}}$  The internuclear distances are not corrected for the increase due to  $\overline{E}_{osc}$  .

$$a = a_{\sigma} \tag{11.317}$$

The semimajor axis, a, is also given by Eq. (11.116) where p=2. The internuclear distance, 2c', which is the distance between the foci is given by Eq. (11.111) where p=2.

$$2c' = a_o (11.318)$$

5 The semiminor axis is given by Eq. (11.112) where p = 2.

$$b = \frac{\sqrt{3}}{2}a_o \tag{11.319}$$

The eccentricity, e, is given by Eq. (11.113).

$$e = \frac{1}{2} {11.320}$$

#### 10 ENERGIES OF THE DIHYDRINO MOLECULAR ION

The potential energy,  $V_e$ , of the electron MO in the field of magnitude twice that of the protons at the foci ( $\xi = 0$ ) is given by Eq. (11.117) where p = 2

$$V_{e} = \frac{-8e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}}$$
(11.321)

The potential energy,  $V_p$ , due to proton-proton repulsion in the field of magnitude twice that 15 of the protons at the foci ( $\xi = 0$ ) is given by Eq. (11.120) where p = 2

$$V_{p} = \frac{2e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}}$$
 (11.322)

The kinetic energy, T, of the electron MO is given by Eq. (11.119) where p=2

$$T = \frac{2h^2}{m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(11.323)

Substitution of a and b given by Eqs. (11.317) and (11.319), respectively, into Eqs. (11.321-20 11.323) and using Eqs. (11.191-11.193) with p=2 gives

$$V_e = \frac{-16e^2}{8\pi\varepsilon_o a_o} \ln 3 = -239.16 \ eV \tag{11.324}$$

$$V_{p} = \frac{4e^{2}}{8\pi\varepsilon_{o}a_{o}} = 54.42 \ eV \tag{11.325}$$

$$T = \frac{8e^2}{8\pi\varepsilon_o a_o} \ln 3 = 119.58 \ eV \tag{11.326}$$

$$E_T = V_a + V_p + T + \overline{E}_{osc} \tag{11.327}$$

$$E_{T} = -2^{2} \left\{ \frac{e^{2}}{8\pi\varepsilon_{o}a_{H}} (4\ln 3 - 1 - 2\ln 3) \left[ 1 + 2\sqrt{\frac{2\hbar\sqrt{\frac{2e^{2}}{4\pi\varepsilon_{o}(2a_{H})^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\}$$

$$= -2^{2} (16.13392 \ eV) - 2^{3} (0.118755 \ eV)$$

$$= -65.49 \ eV$$
(11.328)

where Eqs. (11.324-11.326) are equivalent to Eqs. (11.122-11.124) with p=2. The bond dissociation energy,  $E_D$ , given by Eq. (11.198) with p=2 is the difference between the total 5 energy of the corresponding hydrino atom and  $E_T$  given by Eq. (11.328):

$$E_D = E_T(H(1/p)) - E_T(H_2^+(1/p))$$

$$= 2^2 (2.535 \, eV) + 2^3 (0.118755 \, eV)$$

$$= 11.09 \, eV$$
(11.329)

#### VIBRATION OF THE DIHYDRINO MOLECULAR ION

It can be shown that a perturbation of the orbit determined by an inverse-squared force results 10 in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for  $H_2^+(1/2)$  from Eq. (11.160) is

$$\omega(0) = 2^2 \sqrt{\frac{165.51 \, Nm^{-1}}{\mu}} = 1.78 \, X \, 10^{15} \, radians / s \tag{11.330}$$

wherein p=2. The spring constant, k(0), for  $H_2^+(1/2)$  from Eq. (11.162) is

$$k(0) = 2^{4}165.51 Nm^{-1} = 2648 Nm^{-1}$$
(11.331)

15 The amplitude of oscillation from Eq. (11.164) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2} \left(2^4 \left(165.51\right) N m^{-1} \mu\right)^{1/4}} = \frac{5.952 X 10^{-12} m}{2} = \frac{0.1125 a_o}{2}$$
(11.332)

The vibrational energy,  $E_{vib}(1)$ , for the  $v=1 \rightarrow v=0$  transition given by Eq. (11.166) is

$$E_{vib}(1) = 2^2(0.270 \ eV) = 1.08 \ eV$$
 (11.333)

## THE DIHYDRINO MOLECULE $H_2 \left[ 2c' = \frac{a_b}{\sqrt{2}} \right]$

#### FORCE BALANCE OF THE DIHYDRINO MOLECULE

The force balance equation for the dihydrino molecule  $H_2(1/2)$  is given by Eq. (11.200)

5 where p=2

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{2e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{11.334}$$

which has the parametric solution given by Eq. (11.83) when

$$a = \frac{a_o}{2} \tag{11.335}$$

The semimajor axis, a, is also given by Eq. (11.202) where p=2. The internuclear 10 distance, 2c', which is the distance between the foci is given by Eq. (11.204) where p=2.

$$2c' = \frac{1}{\sqrt{2}}a_o \tag{11.336}$$

The semiminor axis is given by Eq. (11.205) where p = 2.

$$b = c = \frac{1}{2\sqrt{2}}a_o \tag{11.337}$$

The eccentricity, e, is given by Eq. (11.206).

15 
$$e = \frac{1}{\sqrt{2}}$$
 (11.338)

#### ENERGIES OF THE DIHYDRINO MOLECULE

The energies of the dihydrino molecule  $H_2(1/2)$  are given by Eqs. (11.207-11.210) and Eqs. (11.239-11.241) with p=2

20 
$$V_e = \frac{-4e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -271.34 \ eV \tag{11.339}$$

$$V_p = \frac{2}{8\pi\varepsilon_0} \frac{e^2}{\sqrt{a^2 - b^2}} = 76.97 \ eV \tag{11.340}$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 135.67 \text{ eV}$$
 (11.341)

The energy,  $V_m$ , of the magnetic force is

$$V_{m} = \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -67.84 \ eV$$
 (11.342)

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc} \tag{11.343}$$

$$E_{T} = -2^{2} \left\{ \frac{e^{2}}{8\pi\varepsilon_{o}a_{0}} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - \sqrt{2} \right] \left[ 1 + 2\sqrt{\frac{e^{2}}{4\pi\varepsilon_{o}a_{0}^{3}}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right] \right.$$

$$= -2^{2} \left( 31.351 \, eV \right) - 2^{3} \left( 0.326469 \, eV \right)$$

$$= -128.02 \, eV$$

$$(11.344)$$

where Eqs. (11.339-11.342) are equivalent to Eqs. (11.207-11.210) with p=2. The bond 5 dissociation energy,  $E_D$ , given by Eq. (11.252) with p=2 is the difference between the total energy of the corresponding hydrino atoms and  $E_T$  given by Eq. (11.344).

$$E_D = E_T(2H(1/p)) - E_T(H_2(1/p))$$

$$= 2^2 (4.151 \text{ eV}) + 2^3 (0.326469 \text{ eV})$$

$$= 19.22 \text{ eV}$$
(11.345)

#### VIBRATION OF THE DIHYDRINO MOLECULE

10 It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for the  $H_2(1/2)$  from Eq. (11.217) is

$$\omega(0) = 2^2 \sqrt{\frac{k}{\mu}} = 2^2 \sqrt{\frac{621.98 \ Nm^{-1}}{\mu}} 3.45 \ X \ 10^{15} \ radians/s$$
 (11.346)

wherein p=2. The spring constant, k(0), for  $H_2(1/2)$  from Eq. (11.219) is

15 
$$k(0) = 2^4 621.98 \ Nm^{-1} = 9952 \ Nm^{-1}$$
 (11.347)

The amplitude of oscillation from Eq. (11.221) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2} \left(2^4 \left(621.98\right) N m^{-1} \mu\right)^{1/4}} = \frac{4.275 \times 10^{-12} \text{ m}}{2} = \frac{0.08079 a_o}{2}$$
(11.348)

The vibrational energy,  $E_{vib}(1)$ , of  $H_2(1/2)$  from Eq. (11.223) is

$$E_{\nu ib}(1) = 2^2(0.517) \ eV = 2.07 \ eV$$
 (11.349)

#### **GEOMETRY**

The internuclear distance can also be determined geometrically. The spheroidal MO of the hydrogen molecule is an equipotential energy surface, which is an energy minimum surface. For the hydrogen molecule, the electric field is zero for  $\xi > 0$ . Consider two hydrogen atoms 5 A and B approaching each other. Consider that the two electrons form a spheroidal MO as the two atoms overlap, and the charge is distributed such that an equipotential two-dimensional surface is formed. The electric fields of atoms A and B add vectorially as the atoms overlap. The energy at the point of intersection of the overlapping orbitspheres decreases to a minimum as they superimpose and then rises with further overlap. When this energy is a minimum the internuclear distance is determined. It can be demonstrated [33] that when two hydrogen orbitspheres superimpose such that the radial electric field vector from nucleus A and B makes a 45° angle with the point of intersection of the two original orbitspheres, the electric energy of interaction between orbitspheres given by

$$E_{\text{interaction}} = 2 X \frac{1}{2} \varepsilon_o \int \Delta \mathbf{E}^2 dv$$
 (11.350)

15 is a minimum (Figure 7.1 of [33]). The MO is a minimum potential energy surface; therefore, a minimum of energy of one point on the surface is a minimum for the entire surface of the MO. Thus,

$$R_{H_a} = \sqrt{2}a_a = 0.748 \text{\AA} \tag{11.351}$$

The experimental internuclear bond distance is 0.746 Å.

20

#### **DIHYDRINO IONIZATION ENERGIES**

The first ionization energy,  $IP_1$ , of the dihydrino molecule

$$H_2(1/p) \to H_2^+(1/p) + e^-$$
 (11.352)

is given by Eq. (11.244) with p = 2.

25 
$$IP_1 = E_T (H_2^+(1/p)) - E_T (H_2(1/p))$$
 (11.353)

$$IP_1 = 2^2 (15.2171 \ eV) + 2^3 (0.2077 \ eV) = 62.53 \ eV$$
 (11.354)

The second ionization energy,  $IP_2$ , is given by Eq. (11.245) with p=2.

$$IP_2 = 2^2 (16.13392 \ eV) + 2^3 (0.118755 \ eV) = 65.49 \ eV$$
 (11.355)

A hydrino atom can react with a hydrogen, deuterium, or tritium nucleus to form a 30 dihydrino molecular ion that further reacts with an electron to form a dihydrino molecule.

$$H(1/p) + H^+ + e^- \rightarrow H_2(1/p)$$
 (11.356)

The energy released is

$$E = E(H(1/p)) - E_T (11.357)$$

where  $E_T$  is given by Eq. (11.241).

5 A hydrino atom can react with a hydrogen, deuterium, or tritium atom to form a dihydrino molecule.

$$H(1/p) + H \rightarrow H_2(1/p)$$
 (11.358)

The energy released is

$$E = E(H(1/p)) + E(H) - E_T$$
 (11.359)

10 where  $E_T$  is given by Eq. (11.241).

#### SIZES OF REPRESENTATIVE ATOMS AND MOLECULES

#### **ATOMS**

15

Helium Atom (He)

Helium comprises the nucleus at the origin and two electrons as a spherical shell at  $r = 0.567a_0$ .

20 Hydrogen Atom (H[a<sub>H</sub>])

Hydrogen comprises the nucleus at the origin and the electron as a spherical shell at  $r = a_H$ .

Hydrino Atom  $\left(H\left[\frac{a_H}{2}\right]\right)$ 

Hydrino atom (1/2) comprises the nucleus at the origin and the electron as a spherical shell at

$$25 \quad r = \frac{a_H}{2} .$$

#### **MOLECULES**

Hydrogen Molecular Ion  $(\mathbf{H}_{2}[2\mathbf{c}'=2\mathbf{a}_{0}]^{+})$ 

$$a = 2a_0$$

$$b=c=\sqrt{3}a_0$$

$$c' = a_0$$

$$2c'=2a_0$$

5 Hydrogen Molecule  $(H_2[2c'=\sqrt{2}a_o])$ 

$$a = a_0$$

$$b=c=\frac{1}{\sqrt{2}}a_0$$

$$c' = \frac{1}{\sqrt{2}}a_0$$

$$2c' = \sqrt{2}a_0$$

10

Dihydrino Molecular Ion  $(H_2[2c'=a_o]^{\dagger})$ 

$$a = a_0$$

$$b=c=\frac{\sqrt{3}}{2}a_0$$

$$b=c=\frac{1}{2}a_0$$

15 
$$2c' = a_0$$

Dihydrino Molecule ( $\mathbf{H}_2 \left[ 2c' = \frac{1}{\sqrt{2}} \mathbf{a}_o \right]$ )

$$a = \frac{1}{2}a_0$$

$$b=c=\frac{1}{2\sqrt{2}}a_0$$

$$20 \quad c' = \frac{1}{2\sqrt{2}} a_0$$

$$2c' = \frac{1}{\sqrt{2}}a_0$$

## ORTHO-PARA TRANSITION OF HYDROGEN-TYPE MOLECULES

Each proton of hydrogen-type molecules possesses a magnetic moment, which is derived in the Proton and Neutron section and is given by

$$\mu_{P} = \frac{\left(\frac{2}{3}\right)^{2} e\hbar}{2\frac{m_{p}}{2\pi}} \tag{11.360}$$

5 The magnetic moment,  $\mathbf{m}$ , of the proton is given by Eq. (11.360), and the magnetic field of the proton follows from the relationship between the magnetic dipole field and the magnetic moment,  $\mathbf{m}$ , as given by Jackson [34] where  $\mathbf{m} = \mu_p \mathbf{i}_s$ .

$$\mathbf{H} = \frac{\mu_P}{r^3} (\mathbf{i}_r 2 \cos \theta - \mathbf{i}_\theta \sin \theta) \tag{11.361}$$

Multiplication of Eq. (11.361) by the permeability of free space,  $\mu_0$ , gives the magnetic flux, 10 **B**, due to proton one at proton two.

$$\mathbf{B} = \frac{\mu_0 \mu_P}{r^3} (\mathbf{i}_r 2 \cos \theta - \mathbf{i}_\theta \sin \theta)$$
 (11.362)

 $\Delta E_{mag}^{\text{ortho/para}}$ , the energy to flip the orientation of proton two's magnetic moments,  $\mu_p$ , from ortho (parallel magnetic moments) to para (antiparallel magnetic moments) with respect to the direction of the magnetic moment of proton one with corresponding magnetic flux **B** is

15 
$$\Delta E_{mag}^{\text{ortho/para}} = -2\mu_p \mathbf{B} = \frac{-2\mu_0 \mu_p^2}{r^3}$$
 (11.363)

where r is the internuclear distance 2c' where c' is given by Eq. (11.204). Substitution of the internuclear distance into Eq. (11.363) for r gives

$$\Delta E_{mag}^{\text{ortho/para}} = -2\mu_{p} \mathbf{B} = \frac{-2\mu_{0}\mu_{p}^{2} p^{3}}{\left(\sqrt{2}a_{o}\right)^{3}}$$
(11.364)

The frequency, f, can be determined from the energy using the Planck relationship, Eq. 20 (2.18).

$$f = \frac{\Delta E_{mag}^{\text{ortho/para}}}{h} = \frac{\frac{-2\mu_0 \mu_p^2 p^3}{\left(\sqrt{2}a_o\right)^3}}{h}$$
(11.365)

From Eq. (11.365) with p=2, the ortho-para transition energy of the dihydrino molecule is 14.4 MHz.

#### NUCLEAR MAGNETIC RESONANCE SHIFT

The proton gyromagnetic ratio,  $\gamma_p/2\pi$ , is

$$\gamma_P / 2\pi = 42.57602 \ MHz \ T^{-1}$$
 (11.366)

The NMR frequency, f, is the product of the proton gyromagnetic ratio given by Eq. 5 (11.366) and the magnetic flux, B.

$$f = \gamma_P / 2\pi \mathbf{B} = 42.57602 \text{ MHz } T^{-1} \mathbf{B}$$
 (11.367)

A typical flux for a superconducting NMR magnet is 1.5 T. According to Eq. (11.367) this corresponds to a radio frequency (RF) of 63.86403 MHz. With a constant magnetic field, the frequency is scanned to yield the spectrum where the frequency scan is typically achieved using a Fourier transform on the free induction decay signal following a radio frequency pulse. Or, in a less common type of NMR spectrometer, the radiofrequency is held constant (e.g. 60 MHz), the applied magnetic field,  $H_0$  ( $H_0 = \frac{B}{\mu_0}$ ), is varied over a small range, and the frequency of energy absorption is recorded at the various values for  $H_0$ . The spectrum is typically scanned and displayed as a function of increasing  $H_0$ . The protons that absorb energy at a lower  $H_0$  give rise to a downfield absorption peak; whereas, the protons that absorb energy at a higher  $H_0$  give rise to an upfield absorption peak. The electrons of the compound of a sample influence the field at the nucleus such that it deviates slightly from the applied value. For the case that the chemical environment has no NMR effect, the value of  $H_0$  at resonance with the radiofrequency held constant at 60 MHz is

$$\frac{2\pi f}{\mu_0 \gamma_P} = \frac{(2\pi)(60 \text{ MHz})}{\mu_0 42.57602 \text{ MHz } T^{-1}} = H_0$$
 (11.368)

In the case that the chemical environment has a NMR effect, a different value of  $H_0$  is required for resonance. This chemical shift is proportional to the electronic magnetic flux charge at the nucleus due to the applied field, which in the case of each dihydrino molecule is a function of its semimajor and semiminor axes as shown *infra*.

Consider the application of a z-axis-directed uniform external magnetic flux, B<sub>z</sub>, to a dihydrino molecule comprising prolate spheroidal electron MOs with two spin-paired electrons. The diamagnetic reaction current increases or decreases the MO current to counteract any applied flux according to Lenz's law as shown in the Hydrino Hydride Ion Nuclear Magnetic Resonance Shift section. The current of hydrogen-type molecules is along

elliptical orbits parallel to the semimajor axis. Thus, the electronic interaction with the nuclei requires that each nuclear magnetic moment is in the direction of the semiminor axis. Thus, the nuclei are NMR active towards  $\mathbf{B}_z$  when the orientation of the semimajor axis, a, is along the x-axis, and the semiminor axes, b=c, are along the y-axis and z-axis, respectively. The flux is applied over the time interval  $\Delta t = t_i - t_f$  such that the field increases at a rate dB/dt. The electric field,  $\mathbf{E}$ , along a perpendicular elliptic path of the dihydrino MO at the plane z=0 is given by

$$\iint E \cdot ds = \int \frac{dB}{dt} \cdot dA \tag{11.369}$$

The induced electric field must be constant along the path; otherwise, compensating currents 10 would flow until the electric field is constant. Thus, Eq. (11.369) becomes

$$E = \frac{\int \frac{dB}{dt} \cdot dA}{\int \int ds} = \frac{\int \frac{dB}{dt} \cdot dA}{4aE(k)} = \frac{\pi ab \frac{dB}{dt}}{4aE(k)}$$
(11.370)

where E(k) is the elliptic integral given by

$$E(k) = \int_{0}^{\frac{\pi}{2}} \sqrt{1 - k \sin^2 \phi} d\phi = 1.2375$$
 (11.371)

$$k = e = \frac{\sqrt{a^2 - b^2}}{a} = \frac{\sqrt{2}}{2} \tag{11.372}$$

15 the area of an ellipse, A, is

$$A = \pi ab \tag{11.373}$$

the perimeter of an ellipse, s, is

$$s = 4aE(k) \tag{11.374}$$

a is the semimajor axis given by Eq. (11.202), b is the semiminor axis given by Eq. (11.205), and e is the eccentricity given by Eq. (11.206). The acceleration along the path, dv/dt, during the application of the flux is determined by the electric force on the charge density of the electrons:

$$m_e \frac{dv}{dt} = eE = \frac{e\pi ab}{4aE(k)} \frac{dB}{dt}$$
 (11.375)

Thus, the relationship between the change in velocity,  $\nu$ , and the change in B is

$$dv = \frac{e\pi ab}{4aE(k)m_e}dB \tag{11.376}$$

Let  $\Delta v$  represent the net change in v over the time interval  $\Delta t = t_i - t_f$  of the application of the flux. Then,

$$\Delta v = \int_{y_0}^{y_0 + \Delta v} dv = \frac{e\pi ab}{4aE(k)m_e} \int_0^B dB = \frac{e\pi abB}{4aE(k)m_e}$$
(11.377)

The average current, I, of a charge moving time harmonically along an ellipse is

$$I = ef = \frac{ev}{4aE(k)} \tag{11.378}$$

where f is the frequency. The corresponding magnetic moment is given by

$$m = AI = \pi abI = \frac{\pi abev}{4aE(k)}$$
 (11.379)

Thus, from Eqs. (11.377) and (11.379), the change in the magnetic moment,  $\Delta m$ , due to an applied magnetic flux, **B**, is [35]

10 
$$\Delta \mathbf{m} = -\frac{\left(e\pi ab\right)^2 \mathbf{B}}{\left(4aE\left(k\right)\right)^2 m_e}$$
 (11.380)

Next, the contribution from all plane cross sections of the prolate spheroid MO must be integrated along the z-axis. The spheroidal surface is given by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{b^2} = 1 \tag{11.381}$$

The intersection of the plane z = z'  $(-b \le z' \le b)$  with the spheroid determines the curve

15 
$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 - \frac{z^{12}}{b^2}$$
 (11.382)

or

$$\frac{x^2}{a^2 \left(1 - \frac{z^{12}}{b^2}\right)} + \frac{y^2}{b^2 \left(1 - \frac{z^{12}}{b^2}\right)} = 1$$
 (11.383)

Eq. (11.383) is an ellipse with semimajor axis, a', and semiminor axis, b', given by

$$a' = a\sqrt{1 - \frac{z'^2}{b^2}} \tag{11.384}$$

$$20 b' = b\sqrt{1 - \frac{z'^2}{b^2}} (11.385)$$

The eccentricity, e', is given by

$$e' = \frac{\sqrt{a^2 \left(1 - \frac{z'^2}{b^2}\right) - b^2 \left(1 - \frac{z'^2}{b^2}\right)}}{a\sqrt{1 - \frac{z'^2}{b^2}}} = \frac{\sqrt{a^2 - b^2}}{a} = e$$
 (11.386)

where e is given by Eq. (11.372). The area, A', is given by

$$A' = \pi a'b' \tag{11.387}$$

and the perimeter, s', is given by

$$s' = 4a'E(k) = 4aE(k)\sqrt{1 - \frac{z'^2}{b^2}} = s\sqrt{1 - \frac{z'^2}{b^2}}$$
 (11.388)

where s is given by Eq. (11.374). The differential magnetic moment change along the z-axis is

$$d\Delta \mathbf{m} = -\frac{1}{2b} \frac{(e\pi a'b')^2 \mathbf{B}}{(4a'E(k))^2 m_e} dz'$$
 (11.389)

Using Eq. (11.385) for the parameter b', the change in magnetic moment for the dihydrino 10 molecule is given by the integral over  $-b \le b' \le b$ :

$$\Delta \mathbf{m} = -\frac{1}{2b} \int_{-b}^{b} \frac{\left(e\pi a'b\sqrt{1-\frac{z'^2}{b^2}}\right)^2 \mathbf{B}}{\left(4a'E(k)\right)^2 m_e} dz' = -C_1 \frac{1}{m_e} \left(\frac{\pi e}{4E(k)}\right)^2$$
(11.390)

Then, integral to correct for the z-dependence of b' is

$$C_1 = \frac{\int_0^b (b^2 - z^2) dz}{2b} = \frac{2}{3}b^2 = \frac{a_0^2}{3p}$$
 (11.391)

where the semiminor axis,  $b = \frac{a_0}{p\sqrt{2}}$ , given by Eq. (11.205) was used.

The change in magnetic moment would be given by the substitution of Eq. (11.391) into Eq. (11.390), if the change density were constant along the path of Eqs. (11.370) and (11.378), but it is not. The charge density of the MO in rectangular coordinates (Eq. (11.42)) is

$$\sigma = \frac{e}{4\pi abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$
(11.392)

(The mass-density function of an MO is equivalent to its charge-density function where m replaces q of Eq. (11.42)). The equation of the plane tangent to the ellipsoid at the point  $x_0, y_0, z_0$  is

$$X\frac{x_0}{a^2} + Y\frac{y_0}{b^2} + Z\frac{z_0}{c^2} = 1 ag{11.393}$$

5 where X, Y, Z are running coordinates in the plane. After dividing through by the square root of the sum of the squares of the coefficients of X, Y, and Z, the right member is the distance D from the origin to the tangent plane. That is,

$$D = \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$
 (11.394)

so that

$$10 \qquad \sigma = \frac{e}{4\pi abc}D \tag{11.395}$$

In other words, the surface density at any point on the ellipsoidal MO is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin. In order to maintain current continuity, the diamagnetic velocity of Eq. (11.377) must be a constant along any given path integral corresponding to a constant electric field. Consequently, the charge density must be the minimum value of that given by Eq. (11.392). The minimum corresponds to y = b and x = z = 0 such that the charge density is

$$\sigma = \frac{e}{4\pi ab^2} \frac{1}{\sqrt{\frac{0^2}{a^4} + \frac{b^2}{b^4} + \frac{0^2}{b^4}}} = \frac{e}{4\pi ab}$$
 (11.396)

The MO is an equipotential surface, and the current must be continuous over the two-20 dimensional surface. Continuity of the surface current density, K, due to the diamagnetic effect of the applied magnetic field on the MO and the equipotential boundary condition require that the current of each elliptical curve determined by the intersection of the plane z=z' ( $-b \le z' \le b$ ) with the spheroid be the same. The charge density is spheroidally symmetrical about the semimajor axis. Thus,  $\lambda$ , the charge density per unit length along 25 each elliptical path cross section of Eq. (11.383) is given by distributing the surface charge density of Eq. (11.396) uniformly along the z-axis for  $-b \le z' \le b$ . So,  $\lambda(z'=0)$ , the linear charge density  $\lambda$  in the plane z'=0, is

$$\lambda(z'=0) = \frac{\sigma}{\frac{1}{2b}} = \frac{e}{4\pi ab} 2b = \frac{e}{2\pi a}$$
 (11.397)

And, the linear charge density must be equally distributed over each elliptical path cross section corresponding to each plane z = z'. The current is independent of z' when the linear charge density,  $\lambda(z')$ , is normalized for the path length:

5 
$$\lambda(z') = \frac{e}{2\pi a} \frac{4aE(k)}{4a'E(k')} = \frac{e}{2\pi a'}$$
 (11.398)

where the equality of the eccentricities of each elliptical plane cross section given by Eq. (11.386) was used. Substitution of Eq. (11.388) for the corresponding charge density,

 $\frac{e}{4a'E(k)}$ , of Eq. (11.390) and using Eq. (11.391) gives

$$\Delta \mathbf{m} = \frac{2}{3} \frac{e^2 b^2 \mathbf{B}}{4m_e} = \frac{e^2 a_0^2 \mathbf{B}}{12 p^2 m_e}$$
 (11.399)

The two electrons are spin-paired and the velocities are mirror opposites. Thus, the change in velocity of each electron treated individually (Eq. (10.3)) due to the applied field would be equal and opposite. However, as shown in the Three Electron Atom section, the two paired electrons may be treated as one with twice the mass where  $m_e$  is replaced by  $2m_e$  in Eq. (11.399). In this case, the paired electrons spin together about the applied field axis, 15 the z-axis, to cause a reduction in the applied field according to Lenz's law. Thus, from Eq. (11.399), the change in magnetic moment is given by

$$\Delta \mathbf{m} = \frac{e^2 a_0^2 \mathbf{B}}{24 \, p^2 m_e} \tag{11.400}$$

The opposing diamagnetic flux is uniform, parallel, and opposite the applied field as given by Stratton [36]. Specifically, the change in magnetic flux,  $\Delta B$ , at the nucleus due to 20 the change in magnetic moment,  $\Delta m$ , is

$$\Delta \mathbf{B} = \mu_0 A_2 \Delta \mathbf{m} \tag{11.401}$$

where  $\mu_0$  is the permeability of vacuum,

$$A_{2} = \int_{0}^{\infty} \frac{ds}{(s+b^{2})R_{s}}$$
 (11.402)

is an elliptic integral of the second kind given by Whittaker and Watson [37], and

25 
$$R_s = (s+b^2)\sqrt{(s+a^2)}$$
 (11.403)

Substitution of Eq. (11.403) into Eq. (11.402) gives

$$A_2 = \int_0^\infty \frac{ds}{(s+b^2)^2 (s+a^2)^{1/2}}$$
 (11.404)

From integral 154 of Lide [38]:

$$A_{2} = -\left\{\frac{1}{a^{2} - b^{2}} \frac{\sqrt{s + a^{2}}}{s + b^{2}}\right\}_{0}^{\infty} - \frac{1}{2} \frac{1}{a^{2} - b^{2}} \int_{0}^{\infty} \frac{ds}{(s + b^{2})\sqrt{s + a^{2}}}$$
(11.405)

5 The evaluation at the limits of the first integral is

$$-\left\{\frac{1}{a^2-b^2}\frac{\sqrt{s+a^2}}{s+b^2}\right\}_0^\infty = \frac{a}{b^2(a^2-b^2)}$$
(11.406)

From integral #147 of Lide [9], the second integral is:

$$-\frac{1}{2}\frac{1}{a^2-b^2}\int_0^{\infty} \frac{ds}{\left(s+b^2\right)\sqrt{s+a^2}} = \left\{\frac{1}{2}\frac{1}{\left(a^2-b^2\right)^{3/2}}\ln\frac{\sqrt{s+a^2}+\sqrt{a^2-b^2}}{\sqrt{s+a^2}-\sqrt{a^2-b^2}}\right\}_0^{\infty}$$
(11.407)

Evaluation at the limits of the second integral gives

 $-\frac{1}{2} \frac{1}{\left(a^2 - b^2\right)^{3/2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$  (11.408)

Combining Eq. (11.406) and Eq. (11.408) gives

$$A_2 = \frac{a}{b^2 (a^2 - b^2)} - \frac{1}{2 (a^2 - b^2)^{3/2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = \frac{p^3 4}{a_0^3} - \frac{p^3 \sqrt{2}}{a_0^3} \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1}$$
(11.409)

where the semimajor axis,  $a = \frac{a_0}{p}$ , given by Eq. (11.202) and the semiminor axis,  $b = \frac{a_0}{p\sqrt{2}}$ , given by Eq. (11.205) were used.

15 Substitution of Eq. (11.400) and Eq. (11.409) into Eq. (11.401) gives

$$\Delta \mathbf{B} = -\mu_0 \left( \frac{p^3 4}{a_0^3} - \frac{p^3 \sqrt{2}}{a_0^3} \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} \right) \frac{a_0^2 e^2 \mathbf{B}}{24 p^2 m_e}$$
(11.410)

Additionally, it is found both theoretically and experimentally that the dimensions,  $r^2$ , of the molecule corresponding to the area in Eqs. (11.369) and (11.379) used to derived Eq. (11.410) must be replaced by an average,  $\langle r^2 \rangle$ , that takes into account averaging over the orbits isotropically oriented. The correction of 2/3 is given by Purcell [35]. In the case of hydrogen-type molecules, the electronic interaction with the nuclei require that each nuclear magnetic moment is in the direction of the semiminor axis. But free rotation about each of

three axes results in an isotropic averaging of 2/3 where the rotational frequencies of hydrogen-type molecules are much greater than the corresponding NMR frequency (e.g.  $10^{12}$  Hz versus  $10^{8}$  Hz). Thus, Eq. (11.410) gives the absolute upfield chemical shift,  $\frac{\Delta B}{B}$ , of  $H_2$  relative to a bare proton:

$$\frac{\Delta \mathbf{B}}{\mathbf{B}} = \frac{\Delta B}{B} = -\mu_0 \left( \frac{p^3 4}{a_0^3} - \frac{p^3 \sqrt{2}}{a_0^3} \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} \right) \frac{a_0^2 e^2}{36 p^2 m_e}$$

$$= -\mu_0 \left( 4 - \sqrt{2} \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} \right) \frac{p e^2}{36 a_0 m_e}$$

$$= -p28.01 ppm$$
(11.411)

where p=1 for  $H_2$ .

5

It follows from Eqs. (11.202) and (11.411) that the diamagnetic flux (flux opposite to the applied field) at each nucleus is inversely proportional to the semimajor radius,  $a = \frac{u_o}{n}$ . For resonance to occur,  $\Delta H_0$ , the change in applied field from that given by Eq. (11.368), 10 must compensate by an equal and opposite amount as the field due to the electrons of the dihydrino molecule. According to Eq. (11.202), the ratio of the semimajor axis of the dihydrino molecule  $H_2(1/p)$  to that of the hydrogen molecule  $H_2$  is the reciprocal of an integer p. Similarly it is shown in the Hydrino Hydride Ion Nuclear Magnetic Resonance Shift section and previously [39], that according to Eq. (7.87) the ratio of the radius of the 15 hydrino hydride ion  $H^-(1/p)$  to that of the hydride ion  $H^-(1/1)$  is the reciprocal of an integer p. It follows from Eqs. (7.90-7.96) that compared to a proton with no chemical shift, the ratio of  $\Delta H_0$  for resonance of the proton of the hydrino hydride ion  $H^-(1/p)$  to that of the hydride ion  $H^-(1/1)$  is a positive integer. That is, if only the radius is considered, the absorption peak of the hydrino hydride ion occurs at a value of  $\Delta H_0$  that is a multiple of p 20 times the value that is resonant for the hydride ion compared to that of a proton with no shift. However, a hydrino hydride ion is equivalent to the ordinary hydride ion except that it is in a lower energy state. The source current of the state must be considered in addition to the reduced radius.

As shown in the Stability of "Ground" and Hydrino States section, for the below 25 "ground" (fractional quantum number) energy states of the hydrogen atom,  $\sigma_{photon}$ , the two-

dimensional surface charge due to the "trapped photon" at the electron orbitsphere and phase-locked with the electron orbitsphere current, is given by Eqs. (5.08) and (2.11).

$$\sigma_{photon} = \frac{e}{4\pi (r_n)^2} \left[ Y_0^0 (\theta, \phi) - \frac{1}{n} \left[ Y_0^0 (\theta, \phi) + \text{Re} \left\{ Y_t^m (\theta, \phi) e^{i\omega_n t} \right\} \right] \right] \delta(r - r_n)$$

$$n = \frac{1}{p} = 1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots, \qquad (11.412)$$

5 And,  $\sigma_{electron}$  , the two-dimensional surface charge of the electron orbitsphere is

$$\sigma_{electron} = \frac{-e}{4\pi (r_n)^2} \left[ Y_0^0 \left( \theta, \phi \right) + \text{Re} \left\{ Y_\ell^m \left( \theta, \phi \right) e^{i\omega_n t} \right\} \right] \delta(r - r_n)$$
(11.413)

The superposition of  $\sigma_{photon}$  (Eq. (11.412)) and  $\sigma_{electron}$ , (Eq. (11.413)) where the spherical harmonic functions satisfy the conditions given in the Angular Function section is

$$\sigma_{photon} + \sigma_{electron} = \frac{-e}{4\pi (r_n)^2} \left[ \frac{1}{n} Y_0^0 (\theta, \phi) + \left( 1 + \frac{1}{n} \right) \operatorname{Re} \left\{ Y_l^m (\theta, \phi) e^{i\omega_n l} \right\} \right] \delta(r - r_n)$$

$$n = \frac{1}{p} = 1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots,$$
(11.414)

The ratio of the total charge distributed over the surface at the radius of the hydrino hydride ion  $H^-(1/p)$  to that of the hydride ion  $H^-(1/1)$  is an integer p, and the corresponding total source current of the hydrino hydride ion is equivalent to an integer p times that of an electron. The "trapped photon" obeys the phase-matching condition given in Excited States of the One-Electron Atom (Quantization) section, but does not interact with the applied flux directly. Only each electron does; thus,  $\Delta v$  of Eq. (11.377) must be corrected by a factor of 1/p corresponding to the normalization of the electron source current according to the invariance of charge under Gauss' Integral Law. As also shown by Eqs. (7.17-7.23) and (7.87), the "trapped photon" gives rise to a correction to the change in magnetic moment due to the interaction of each electron with the applied flux. The correction factor of 1/p consequently cancels the NMR effect of the reduced radius which is consistent with general observations on diamagnetism [40]. It follows that the same result applies in the case of Eq. (11.411) for  $H_2(1/p)$  wherein the coordinates are ellipsoidal rather than spherical.

The cancellation of the chemical shift due to the reduced radius or the reduced 25 semiminor and semimajor axes in the case of  $H^-(1/p)$  and  $H_2(1/p)$ , respectively, by the corresponding source current is exact except for an additional relativistic effect. The relativistic effect for  $H^-(1/p)$  arises due to the interaction of the currents corresponding to

the angular momenta of the "trapped photon" and the electrons and is analogous to that of the fine structure of the hydrogen atom involving the  ${}^2P_{3/2}$ — ${}^2P_{1/2}$  transition. The derivation follows that of the fine structure given in the Spin-Orbital Coupling section.

 $\frac{e}{m_e}$  of the electron, the electron angular momentum of  $\hbar$ , and the electron magnetic

5 momentum of  $\mu_B$  are invariant for any electronic state. The same applies for the paired electrons of hydrino hydride ions. The condition that flux must be linked by the electron in units of the magnetic flux quantum in order to conserve the invariant electron angular momentum of  $\hbar$  gives the additional chemical shift due to relativistic effects. Using Eqs. (2.159-2.160), Eq. (2.166) may be written as

10 
$$E_{s/o} = \frac{\alpha \pi \mu_0 e^2 \hbar^2}{m_e^2 r^3} \sqrt{\frac{3}{4}} = \alpha 2\pi 2 \frac{e\hbar}{2m_e} \frac{\mu_0 e\hbar}{2m_e a_0^3} \sqrt{\frac{3}{4}} = \alpha 2\pi 2\mu_B B$$
 (11.415)

From Eq. (11.415) and Eq. (1.205), the relativistic stored magnetic energy contributes a factor of  $\alpha 2\pi$  In spherical coordinates, the relativistic change in flux  $\Delta \mathbf{B}_{SR}$  may be calculated using Eq. (7.95) and the relativistic factor of  $\gamma_{SR} = 2\pi\alpha$  which is the same as that given by Eq. (1.229):

15 
$$\Delta \mathbf{B}_{SR} = -\gamma_{SR} \mu_0 \frac{\Delta m}{r_n^3} (\mathbf{i}_r \cos \theta - \mathbf{i}_\theta \sin \theta) = -2\pi \alpha \mu_0 \frac{\Delta m}{r_n^3} (\mathbf{i}_r \cos \theta - \mathbf{i}_\theta \sin \theta)$$
 (11.416) for  $r < r_n$ 

The stored magnetic energy term of the electron g factor of each electron of a dihydrino molecule is the same as that of a hydrogen atom since  $\frac{e}{m_e}$  is invariant and the

invariant angular momentum and magnetic moment of the former are also  $\hbar$  and  $\mu_B$ , 20 respectively, as given in the Magnetic Moment of an Ellipsoidal MO and Magnetic Field of an Ellipsoidal MO sections. Thus, the corresponding correction in ellipsoidal coordinates follows from Eq. (2.166) wherein the result of the length contraction for the circular path in spherical coordinates is replaced by that of the elliptical path.

The only position on the elliptical path at which the current is perpendicular to the 25 radial vector defined by the central force of the protons is at the semimajor axis. It was shown in the Special Relativistic Correction to the Ionization Energies section that when the condition that the electron's motion is tangential to the radius is met, the radius is Lorentzian invariant. That is, for the case that k is the lightlike  $k^0$ , with  $k = \omega_n/c$ , a is invariant. In

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the case of a spherically symmetrical MO such as the case of the hydrogen atom, it was also shown that this condition determines that the electron's angular momentum of  $\hbar$ ,  $\frac{e}{m}$  of Eq. (1.110), and the electron's magnetic moment of a Bohr magneton,  $\mu_B$ , are invariant. The effect of the relativistic length contraction and time dilation for constant spherical motion is a 5 change in the angle of motion with a corresponding decrease in the electron wavelength. The angular motion becomes projected onto the radial axis which contracts, and the extent of the decrease in the electron wavelength and radius due to the electron motion in the laboratory

$$\lambda = 2\pi r' \sqrt{1 - \left(\frac{v}{c}\right)^2} \sin\left[\frac{\pi}{2} \left(1 - \left(\frac{v}{c}\right)^2\right)^{3/2}\right] + r' \cos\left[\frac{\pi}{2} \left(1 - \left(\frac{v}{c}\right)^2\right)^{3/2}\right]$$
(11.417)

10 and

inertial frame are given by

$$r = r' \left[ \sqrt{1 - \left(\frac{v}{c}\right)^2} \sin \left[ \frac{\pi}{2} \left( 1 - \left(\frac{v}{c}\right)^2 \right)^{3/2} \right] + \frac{1}{2\pi} \cos \left[ \frac{\pi}{2} \left( 1 - \left(\frac{v}{c}\right)^2 \right)^{3/2} \right] \right]$$
 (11.418)

respectively. Then, the relativistic factor  $\gamma^*$  is

$$\gamma' = \frac{2\pi}{2\pi\sqrt{1 - \left(\frac{v}{c}\right)^2 \sin\left[\frac{\pi}{2}\left(1 - \left(\frac{v}{c}\right)^2\right)^{3/2}\right] + \cos\left[\frac{\pi}{2}\left(1 - \left(\frac{v}{c}\right)^2\right)^{3/2}\right]}}$$
(11.419)

where the velocity is given by Eq. (1.56) with the radius given by Eq. (1.233).

Each point or coordinate position on the continuous two-dimensional electron MO of 15 the dihydrino molecule defines an infinitesimal mass-density element which moves along an elliptical orbit of a spheroidal MO in such a way that its eccentric angle,  $\theta$ , changes at a constant rate. That is  $\theta = \omega t$  at time t where  $\omega$  is a constant, and

$$r(t) = ia\cos\omega t + jb\sin\omega t \tag{11.420}$$

20 is the parametric equation of the ellipse. Next, special relativistic effects on distance and time are considered. The parametric radius, r(t), is a minimum at the position of the semiminor axis of length b, and the motion is transverse to the radial vector. Since the angular momentum of  $\hbar$  is constant, the electron wavelength without relativistic correction is given by

$$25 2\pi b = \lambda = \frac{h}{mv} (11.421)$$

such that the angular momentum, L, is given by

$$L = r \times mv = bmv = \hbar \tag{11.422}$$

The nonradiation and the  $\hbar$ ,  $\frac{e}{m_e}$ , and  $\mu_B$  invariance conditions require that the angular

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frequencies,  $\omega_s$  and  $\omega_e$ , for spherical and ellipsoidal motion, respectively, are

$$\omega_s = \frac{\hbar}{m_e r^2} = \frac{\frac{\pi L}{m_e}}{A} \tag{11.423}$$

5 and

$$\omega_e = \frac{\pi\hbar}{m_e A} = \frac{\hbar}{m_e ab} \tag{11.424}$$

where A is the area of the closed orbit, the area of an ellipse given by Eq. (11.373). Since the angular frequency  $\omega_s$  has the form as  $\omega_s$ , the time dilation corrections are equivalent, where the correction for  $\omega_s$  is given in the Special Relativistic Correction to the Ionization Energies 10 section. Since the semimajor axis, a, is invariant, but b undergoes length contraction, the relationship between the velocity and the electron wavelength at the semiminor axis from Eq. (11.417) and Eq. (11.421) is

$$\lambda = 2\pi b \sqrt{1 - \left(\frac{v}{c}\right)^2} \sin \left[\frac{\pi}{2} \left(1 - \left(\frac{v}{c}\right)^2\right)^{3/2}\right] + a \cos \left[\frac{\pi}{2} \left(1 - \left(\frac{v}{c}\right)^2\right)^{3/2}\right]$$
 (11.425)

where  $\lambda \to a$  as  $v \to c$  replaces the spherical coordinate result of  $\lambda \to r'$  as  $v \to c$ . Thus, in the electron frame at rest v = 0, and, Eq. (11.425) becomes

$$\lambda' = 2\pi b \tag{11.426}$$

In the laboratory inertial frame for the case that v = c in Eq. (11.425),  $\lambda$  is

$$\lambda = a \tag{11.427}$$

Thus, using Eqs. (11.426) and (11.427), the relativistic factor,  $\gamma^*$ , is

$$\gamma^{\bullet} = \frac{\lambda}{\lambda'} = \frac{a}{2\pi b} \tag{11.428}$$

From Eqs. (11.417-11.419) and Eq. (11.428), the relativistic diamagnetic effect of the inverse integer radius of  $H_2(1/p)$  compared to  $H_2$ , each with ellipsoidal MOs, is equivalent to the ratio of the semiminor and semimajor axes times the correction for the spherical orbital case given in Eq. (11.416). From the mass (Eq. (2.165)) and radius corrections (Eq. (2.163)) in Eq. (2.166), the relativistic stored magnetic energy contributes a factor  $\gamma_{SR}$  of

$$\gamma_{SR} = 2\pi\alpha \left(\frac{b}{a}\right)^2 = \pi\alpha \tag{11.429}$$

Thus, from Eqs. (11.401), (11.416), and (11.429), the relativistic change in flux,  $\Delta \mathbf{B}_{SR}$ , for the dihydrino molecule  $H_2(1/p)$  is

$$\Delta \mathbf{B}_{sp} = -\gamma_{sp}\mu_0 A_2 \Delta \mathbf{m} = -\pi \alpha \mu_0 A_2 \Delta \mathbf{m} \tag{11.430}$$

5 Thus, using Eq. (11.411) and Eq. (11.430), the upfield chemical shift,  $\frac{\Delta B_{SR}}{B}$ , due to the relativistic effect of the molecule  $H_2(1/p)$  corresponding to the lower-energy state with principal quantum energy state p is given by

$$\frac{\Delta B_{SR}}{B} = -\mu_0 \pi \alpha \left( 4 - \sqrt{2} \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} \right) \frac{pe^2}{36a_0 m_e}$$
 (11.431)

The total shift,  $\frac{\Delta B_T}{B}$ , for  $H_2(1/p)$  is given by the sum of that of  $H_2$  given by Eq. (11.411) 10 with p=1 plus that given by Eq. (11.431):

$$\frac{\Delta B_T}{B} = -\mu_0 \left( 4 - \sqrt{2} \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} \right) \frac{e^2}{36a_0 m_e} (1 + \pi \alpha p)$$
 (11.432)

$$\frac{\Delta B_T}{R} = -(28.01 + 0.64 \, p) \, ppm \tag{11.433}$$

where p = integer > 1.

 $H_2$  has been characterized by gas phase  $^1H$  NMR. The experimental absolute resonance shift of gas-phase TMS relative to the proton's gyromagnetic frequency is -28.5 ppm [30].  $H_2$  was observed at 0.48 ppm compared to gas phase TMS set at 0.00 ppm [31]. Thus, the corresponding absolute  $H_2$  gas-phase resonance shift of -28.0 ppm (-28.5 + 0.48) ppm was in excellent agreement with the predicted absolute gas-phase shift of -28.01 ppm given by Eq. (11.411).

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## **Section II**

# GENERAL DIATOMIC AND POLYATOMIC MOLECULAR IONS AND MOLECULES

5 Non-hydrogen diatomic and polyatomic molecular ions and molecules can be solved using the same principles as those used to solve hydrogen molecular ions and molecules wherein the hydrogen molecular orbitals (MOs) and hydrogen atomic orbitals serve as basis functions for the MOs of the general diatomic and polyatomic molecular ions or molecules. The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) 10 correspond to an orbital solution of the Newtonian equation of motion in an inverse-radiussquared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of h. Energy of the MO must be matched to that of the outermost atomic orbital of a bonding heteroatom in the case where a minimum energy is achieved with a direct bond to the atomic orbital (AO). In the case that an independent 15 MO is formed, the AO force balance causes the remaining electrons to be at lower energy and a smaller radius. The atomic orbital may hybridize in order to achieve a bond at an energy minimum. At least one molecule or molecular ion representative of each of these cases was solved. Specifically, the results of the determination of bond parameters of  $H_3^+$ ,  $D_3^+$ , OH, OD,  $H_2O$ ,  $D_2O$ , NH, ND,  $NH_2$ ,  $ND_2$ ,  $NH_3$ ,  $ND_3$ , CH, CD,  $CH_2$ ,  $CH_3$ ,  $CH_4$ ,  $N_2$ , 20  $O_2$ ,  $F_2$ ,  $Cl_2$ , CN, CO, and NO are given in Table 13.1. The calculated results for homoand hetero-diatomic radicals and molecules, and polyatomic molecular ions and molecules are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

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#### TRIATOMIC MOLECULAR HYDROGEN-TYPE ION $(H_3^*)$

The polyatomic molecular ion  $H_3^+(1/p)$  is formed by the reaction of a proton with a hydrogen-type molecule

$$H_2(1/p) + H^+ \to H_3^+(1/p)$$
 (13.1)

30 and by the exothermic reaction

$$H_{2}^{+}(1/p) + H_{2}(1/p) \to H_{3}^{+}(1/p) + H(1/p)$$
(13.2)

## FORCE BALANCE OF $H_3^+$ -TYPE MOLECULAR IONS

 $H_3^+(1/p)$ -type molecular ions comprise two indistinguishable spin-paired electrons bound 5 by three protons. The ellipsoidal molecular orbital (MO) satisfies the boundary constraints as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. Since the protons are indistinguishable, ellipsoidal MOs about each pair of protons taken one at a time are indistinguishable.  $H_3^+(1/p)$  is then given by a superposition or linear combinations of three equivalent ellipsoidal MOs that form a equilateral triangle where the points of contact 10 between the prolate spheroids are equivalent in energy and charge density. The outer perimeter of the superposition of three prolate spheroids is the  $H_3^+(1/p)$  MO with the protons at the foci that bind and maintain the electron MO.

As in the case for  $H_2^+(1/p)$  and  $H_2(1/p)$  shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section, the stability of  $H_3^+(1/p)$  is due to the 15 dependence of the charge density of the distance D from the origin to the tangent plane. That is,

$$D = \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$
 (13.3)

so that

$$\sigma = \frac{e}{4\pi a h^2} D \tag{13.4}$$

- 20 In other words, the surface density at any point on a charged ellipsoidal conductor is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin. This distribution places the charge closest to the protons to give a minimum energy.
- The balanced forces also depend on D as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The D-dependence of the charge density as well as the centrifugal and Coulombic central field of two nuclei at the foci of the ellipsoid applies to each ellipsoid which is given from any other by a rotation of  $|\phi| = \frac{\pi}{3}$  about an axis at a focus

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that is perpendicular to the plane of the equilateral triangle defined by the three foci. Since the centrifugal, Coulombic, and magnetic forces relate mass and charge densities which are interchangeable by the ratio  $e/m_e$ , the conditions at any point on any given ellipsoid is applicable to any other point on the ellipsoid. Furthermore, this condition can be generalized to any point of the other members of the set of three ellipsoids due to equivalence. As a further constraint to maintain the force balance between the three protons and the  $H_3^+(1/p)$  MO comprising the superposition of the three  $H_2(1/p)$ -type ellipsoidal MOs, the total charge of the two electrons must be normalized over the three basis set  $H_2(1/p)$ -type ellipsoidal MOs. In this case, the parameters of each basis element  $H_2(1/p)$ -type ellipsoidal MO is solved, and the energies are given by the electron charge where it appears multiplied by a factor of 3/2 (three MOs normalized by the total charge of two electrons).

Consider each  $H_2(1/p)$ -type ellipsoidal MO. At each point on the  $H_3^+(1/p)$  MO, the electron experiences a centrifugal force, and the balancing centripetal force (on each electron) is produced by the electric force between the electron and the ellipsoidal electric field and the radiation-reaction-type magnetic force between the two electrons causing the electrons to pair. The force balance equation derived in Force Balance of Hydrogen-Type Molecules section is given by Eq. (11.200):

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{p e^2}{8\pi \varepsilon_e a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.5}$$

$$\frac{2a_0}{pa} - \frac{a_0}{pa} = 1 \tag{13.6}$$

20

$$a = \frac{a_0}{p} \tag{13.7}$$

Substitution of Eq. (13.7) into Eq. (11.79) is

$$c' = \frac{1}{p\sqrt{2}}a_0 \tag{13.8}$$

The internuclear distance given by multiplying Eq. (13.8) by two is

$$2c' = \frac{a_0\sqrt{2}}{p} \tag{13.9}$$

25 Substitution of Eqs. (13.7-13.8) into Eq. (11.80) is

$$b = c = \frac{1}{p\sqrt{2}}a_0 \tag{13.10}$$

103 Substitution of Eqs. (13.7-13.8) into Eq. (11.67) is

$$e = \frac{1}{\sqrt{2}} \tag{13.11}$$

Using the parameters given by Eqs. (13.7-13.11), the resulting  $H_3^+(1/p)$  MO comprising the superposition of three  $H_2(1/p)$ -type ellipsoidal MOs is shown in Figure 6. The outer surface of the superposition comprises charge density of the MO. The equilateral triangular structure was confirmed experimentally [1]. The  $H_3^+(1/p)$  MO having no distinguishable electrons is consistent with the absence of strong excited stated observed for  $H_3^+$  [1]. It is also consistent with the absence of a permanent dipole moment [1].

## 10 ENERGIES OF $H_3^+$ -TYPE MOLECULAR IONS

The due to the equivalence of the  $H_2(1/p)$ -type ellipsoidal MOs and the linear superposition of their energies, the energy components defined previously for the molecule, Eqs. (11.207-11.212) apply in the case of the corresponding  $H_3^+(1/p)$  molecular ion. And, each molecular energy component is given by the integral of corresponding force in Eq. (13.5). Each energy component is the total for the two equivalent electrons with the exception that the total charge of the two electrons is normalized over the three basis set  $H_2(1/p)$ -type ellipsoidal MOs. Thus, the energies are those given for  $H_2(1/p)$  in the Energies of Hydrogen-Type Molecules section with the electron charge, where it appears, multiplied by a factor of 3/2. In addition, the three sets of equivalent proton-proton pairs 20 give rise to a factor of three times the proton-proton repulsion energy given by Eq. (11.208). The parameters a and b are given by Eqs. (13.7) and (13.10), respectively.

$$V_{e} = \frac{3}{2} \frac{-2pe^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}}$$
(13.12)

$$V_p = 3 \frac{p}{8\pi\varepsilon_0} \frac{e^2}{\sqrt{a^2 - b^2}} \tag{13.13}$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(13.14)

25 The energy,  $V_m$ , corresponding to the magnetic force of Eq. (13.5) is

$$V_{m} = \frac{3}{2} \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}$$
(13.15)

$$E_T = V_a + T + V_m + V_p (13.16)$$

$$E_T = -\frac{e^2}{8\pi\varepsilon_0 a_0} \left[ \left( 3p^2\sqrt{2} - p^2\sqrt{2} + 3\frac{p^2\sqrt{2}}{4} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - 3p^2\sqrt{2} \right] = -p^2 35.54975 \ eV$$

(13.17)

5 where the charge e appears in the magnetic energy  $V_m$  according to Eqs. (7.14-7.24) as discussed in the Force Balance of Hydrogen-Type Molecules section.

#### VIBRATION OF $H_3^+$ -TYPE MOLECULAR IONS

The vibrational energy levels of  $H_3^*$ -type molecular ions may be solved as three equivalent 10 coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

#### 15 THE DOPPLER ENERGY TERM OF $H_3^+$ -TYPE MOLECULAR IONS

As shown in the Vibration of Hydrogen-type Molecular Ions section, the electron orbiting the nuclei at the foci of an ellipse may be perturbed such that a stable reentrant orbit is established that gives rise to a vibrational state corresponding to time harmonic oscillation of the nuclei and electron. The perturbation is caused by a photon that is resonant with the 20 frequency of oscillation of the nuclei wherein the radiation is electric dipole with the corresponding selection rules.

Oscillation may also occur in the transition state. The perturbation arises from the decrease in internuclear distance as the molecular bond forms. Relative to the unperturbed case given in the Force Balance of Hydrogen-type Molecular Ions section, the reentrant orbit may give rise to a decrease in the total energy while providing a transient kinetic energy to the vibrating nuclei. However, as an additional condition for stability, radiation must be considered. A nonradiative state must be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. The radiation reaction force due to the vibration of  $H_2^+(1/p)$  and  $H_2(1/p)$  in the transition state

was derived in the Doppler Energy Term of Hydrogen-type Molecular Ions section and the Doppler Energy Term of Hydrogen-type Molecules section, respectively, and corresponds to a Doppler energy,  $E_D$ , that is dependent on the motion of the electron and the nuclei. The radiation reaction force in the case of the vibration of  $H_3^+(1/p)$  in the transition state also corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. Here, a nonradiative state must also be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. Typically, a third body is required to form  $H_3^+$ -type molecular ions. For example, the exothermic chemical reaction of H + H to form  $H_2$  does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body, M, to remove the bond energy- $H + H + M \rightarrow H_2 + M^*$  [3]. The third body distributes the energy from the exothermic reaction, and the end result is the  $H_2$  molecule and an increase in the temperature of the system. Thus, a third body removes the energy corresponding to the additional force term given by Eq. (11.180).

The kinetic energy of the transient vibration is derived from the corresponding central forces. From Eqs. (13.5) and (13.12), the central force terms between the electron MO and the protons of each of the three  $H_2(1/p)$ -type ellipsoidal MOs are

$$f(a) = -\frac{3}{2} \frac{pe^2}{4\pi\varepsilon a^2} \tag{13.18}$$

and

20

$$f'(a) = \frac{3}{2} \frac{2pe^2}{4\pi\varepsilon a^3} \tag{13.19}$$

Thus, using Eqs. (11.136) and (13.18-13.19), the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\frac{3}{2} \frac{pe^2}{4\pi\varepsilon_o \left(\frac{a_0}{p}\right)^3}}{m_e}} = p^2 5.06326 \, X \, 10^{16} \, rad/s \tag{13.20}$$

where the semimajor axis, a, is  $a = \frac{a_0}{p}$  according to Eq. (13.7). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

25 
$$\vec{E}_K = \hbar \omega = \hbar p^2 5.06326 \, X \, 10^{16} \, rad \, / \, s = p^2 33.3273 \, eV$$
 (13.21)

In Eq. (11.181), substitution of the total energy of the  $H_3^+$ -type molecular ion,  $E_7$ , (Eq. (13.17)) for  $E_{lo}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.21) for  $\overline{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit.

$$\widetilde{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -35.54975 p^2 \ eV \sqrt{\frac{2e(p^2 33.3273 \ eV)}{m_e c^2}} = -p^3 0.406013 \ eV \quad (13.22)$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the

5 The total energy of the  $H_3^+$ -type molecular ion is decreased by  $\overline{E}_n$ .

transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons,  $\overline{E}_{Kvib}$ , is 1/2 10 of the vibrational energy of the  $H_3^+$ -type molecular ion given by Eq. (11.148). The decrease in the energy of the molecular ion due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  and  $\overline{E}_{Kvib}$ . Using Eq. (13.22) and the experimental

 $\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar p^2 \sqrt{\frac{k}{\mu}}$ 15 (13.23)

vibrational energy  $H_3^+$  of  $E_{vib} = 2521.31 \text{ cm}^{-1} = 0.312605 \text{ eV}$  [1] gives

$$\overline{E}_{osc} = -p^3 0.406013 \ eV + \frac{1}{2} p^2 (0.312605 \ eV)$$
 (13.24)

The reentrant orbit for the binding of a proton to  $H_2(1/p)$  causes two bonds to oscillate by increasing and decreasing in length along opposite sides of the equilateral triangle at a relative phase angle of 180°. Since the vibration and reentrant oscillation is along two 20 lengths of the equilateral triangular MO with E symmetry,  $\overline{E}_{osc}$  for  $H_3^+(1/p)$ ,  $\overline{E}_{osc}(H_3^+(1/p))$ , is:

$$\overline{E}_{osc}(H_3^+(1/p)) = 2\left(\overline{E}_D + \frac{1}{2}\hbar p^2 \sqrt{\frac{k}{\mu}}\right) 
= 2\left(-p^3 0.406013 \ eV + \frac{1}{2}p^2 (0.312605 \ eV)\right)$$
(13.25)

To the extent that the MO dimensions are the same, the electron reentrant orbital energies,  $\overline{E}_{K}$ , are the same independent of the isotope of hydrogen, but the vibrational

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energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.22), Eq. (13.25), and the experimental vibrational energy  $D_3^+$  of  $E_{vlb} = 1834.67 \text{ cm}^{-1} = 0.227472 \text{ eV}$  [1], the corresponding  $\overline{E}_{osc}(D_3^+(1/p))$  is

$$\overline{E}_{osc}(D_3^+(1/p)) = 2\left(-p^3 0.406013 \ eV + \frac{1}{2} p^2 (0.227472 \ eV)\right)$$
(13.26)

TOTAL AND BOND ENERGIES OF  $H_3^+(1/p)$ - AND  $D_3^+(1/p)$ -TYPE MOLECULAR IONS

The total energy of the  $H_3^+(1/p)$ -type molecular ion is given by the sum of  $E_T$  (Eqs. (13.16-10 13.17)) and  $\overline{E}_{osc}(H_3^+(1/p))$  given Eqs. (13.20-13.25). Thus, the total energy of  $H_3^+(1/p)$  having a central field of +pe at each focus of the prolate spheroid molecular orbital including the Doppler term is

$$E_{T} = V_{e} + T + V_{m} + V_{p} + \overline{E}_{osc} (H_{3}^{+} (1/p))$$
(13.27)

$$E_{T} = -p^{2} \left\{ \frac{e^{2}}{8\pi\varepsilon_{0}a_{0}} \left[ \left( 3\sqrt{2} - \sqrt{2} + \frac{3\sqrt{2}}{4} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - 3\sqrt{2} \right] \left[ 1 + 2p \sqrt{\frac{2\hbar\sqrt{\frac{3}{2}\frac{e^{2}}{4\pi\varepsilon_{0}}a_{0}^{3}}}{\frac{m_{e}}{m_{e}}c^{2}}} \right] - 2\left( \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \right]$$

$$= -p^{2}35.54975 - 2p^{3}0.406013 \ eV + 2p^{2} \left( \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right)$$

$$(13.28)$$

From Eqs. (13.24-13.25) and (13.27-13.28), the total energy of the  $H_3^+$ -type molecular ion is

$$E_{T} = -p^{2}35.54975 \ eV + \overline{E}_{osc} \left( H_{3}^{+} \left( 1/p \right) \right)$$

$$= -p^{2}35.54975 - 2p^{3}0.406013 \ eV + 2 \left( \frac{1}{2} p^{2} \left( 0.312605 \ eV \right) \right)$$

$$= -p^{2}35.23714 \ eV - p^{3}0.812025 \ eV$$
(13.29)

The total energy of the  $D_3^+$ -type molecular ion is given by the sum of  $E_T$  (Eq. (13.17)) and 20  $\overline{E}_{asc}(D_3^+(1/p))$  given by Eq. (13.26):

$$E_{T} = -p^{2}35.54975 \ eV + \overline{E}_{osc} \left( D_{3}^{+} \left( 1/p \right) \right)$$

$$= -p^{2}35.54975 - 2p^{3}0.406013 \ eV + 2 \left( \frac{1}{2} p^{2} \left( 0.227472 \ eV \right) \right)$$

$$= -p^{2}35.32227 \ eV - p^{3}0.812025 \ eV$$
(13.30)

The bond dissociation energy,  $E_D$ , is the difference between the total energy of the corresponding hydrogen molecule and  $E_T$ 

$$E_D = E(H_2(1/p)) - E_T \tag{13.31}$$

5 where  $E(H_2(1/p))$  is given by Eq. (11.241):

$$E(H_2(1/p)) = -p^2 31.351 \, eV - p^3 0.326469 \, eV \tag{13.32}$$

and  $E(D_2(1/p))$  is given by Eq. (11.242):

$$E(D_2(1/p)) = -p^2 31.4345 \ eV - p^3 0.326469 \ eV \tag{13.33}$$

The  $H_3^+$  bond dissociation energy,  $E_D$ , is given by Eqs. (13.31-13.32) and (13.29):

$$E_D = -p^2 31.351 \ eV - p^3 0.326469 \ eV - E_T$$

$$= -p^2 31.351 \ eV - p^3 0.326469 \ eV - \left(-p^2 35.23714 \ eV - p^3 0.812025 \ eV\right) (13.34)$$

$$= p^2 3.88614 \ eV + p^3 0.485556 \ eV$$

The  $D_3^+$  bond dissociation energy,  $E_D$ , is given by Eqs. (13.31), (13.33), and (13.30):

$$\begin{split} E_D &= -p^2 31.4345 \ eV - p^3 0.326469 \ eV - E_T \\ &= -p^2 31.4345 \ eV - p^3 0.326469 \ eV - \left( -p^2 35.32227 \ eV - p^3 0.812025 \ eV \right) \\ &= p^2 3.88777 \ eV + p^3 0.485556 \ eV \end{split}$$

(13.35)

# 15 THE H<sub>3</sub> MOLECULAR ION

## FORCE BALANCE OF THE $H_3^+$ MOLECULAR ION

The force balance equation for  $H_3^+$  is given by Eq. (13.5) where p=1

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi \varepsilon_e a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.36}$$

20 which has the parametric solution given by Eq. (11.83) when

$$a = a_o \tag{13.37}$$

The semimajor axis, a, is also given by Eq. (13.7) where p=1. The internuclear distance, 2c', which is the distance between the foci is given by Eq. (13.9) where p=1.

$$2c' = \sqrt{2}a_a \tag{13.38}$$

The semiminor axis is given by Eq. (13.10) where p = 1.

$$5 b = \frac{1}{\sqrt{2}}a_o (13.39)$$

The eccentricity, e, is given by Eq. (13.11).

$$e = \frac{1}{\sqrt{2}} \tag{13.40}$$

### ENERGIES OF THE H<sub>3</sub> MOLECULAR ION

10 The energies of  $H_3^+$  are given by Eqs. (13.12-13.15) where p=1

$$V_e = \frac{3}{2} \frac{-2e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -101.7538 \, eV$$
 (13.41)

$$V_p = 3 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 57.7245 \ eV \tag{13.42}$$

$$T = \frac{\hbar^2}{2m \cdot a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 33.9179 \text{ eV}$$
 (13.43)

The energy,  $V_m$ , of the magnetic force is

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$$V_m = \frac{3}{2} \frac{-\hbar^2}{4m_a a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -25.4384 \text{ eV}$$
 (13.44)

The Doppler terms,  $\overline{E}_{osc}\left(H_3^+\left(1/p\right)\right)$  and  $\overline{E}_{osc}\left(D_3^+\left(1/p\right)\right)$  are given by Eqs. (13.25) and (13.26), respectively, where p=1

$$\overline{E}_{osc}(H_2^+) = 2(\overline{E}_D + \overline{E}_{Kvib}) 
= 2\left(-0.406013 \ eV + \frac{1}{2}(0.312605 \ eV)\right) 
= -0.499420 \ eV$$
(13.45)

$$\overline{E}_{osc}(D_2) = 2\left(-0.406013 \ eV + \frac{1}{2}(0.227472 \ eV)\right)$$

$$= -0.584553 \ eV$$
(13.46)

20 The total energy,  $E_T$ , for  $H_3^+$  given by Eqs. (13.27-13.29) is

$$E_{T} = -\left\{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}\left[\left(3\sqrt{2} - \sqrt{2} + \frac{3\sqrt{2}}{4}\right)\ln\frac{\sqrt{2} + 1}{\sqrt{2} - 1} - 3\sqrt{2}\right]\left[\frac{2\hbar\sqrt{\frac{3}{2}\frac{e^{2}}{4\pi\varepsilon_{0}}a_{0}^{3}}}{m_{e}}\right] - 2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\right\}$$

$$= -35.54975 - 2\left(0.406013\ eV\right) + 2\left(\frac{1}{2}\left(0.31260516\ eV\right)\right)$$

$$= -36.049167\ eV$$
(13.47)

From Eqs. (13.27-13.28) and (13.30), the total energy,  $E_T$ , for  $D_3^+$  is

$$E_T = -35.54975 - 2(0.406013 \, eV) + 2\left(\frac{1}{2}(0.227472 \, eV)\right)$$

$$= -36.134300 \, eV$$
(13.48)

5 The bond dissociation energy,  $E_D$ , is the difference between the total energy of  $H_2$  or  $D_2$  and  $E_T$ . The  $H_3^+$  molecular bond dissociation energy,  $E_D$ , given by the difference between the experimental total energy of  $H_2$  [5-7] <sup>1</sup> and the total energy of  $H_3^+$  (Eqs. (13.29) where p=1 and (13.47)) is

$$E_D = -31.675 \ eV - (-36.049167 \ eV)$$
  
= 4.374167 \ eV

10 The  $H_3^+$  bond dissociation energy,  $E_D$ , given by Eq. (13.34) where p=1 is

$$E_D = 3.88614 \ eV + 0.485556 \ eV$$
  
= 4.37170 \ eV (13.50)

The experimental bond dissociation energy of  $H_3^+$  [8] is

$$E_D = 4.373 \ eV \tag{13.51}$$

The difference between the results of Eqs. (13.49) and (13.50) is within the experimental and propagated errors in the different calculations. The calculated results are based on first principles and given in closed-form equations containing fundamental constants only. The agreement between the experimental and calculated results for the  $H_3^+$  bond dissociation energy is excellent.

<sup>&</sup>lt;sup>1</sup> The experimental total energy of the hydrogen molecule is given by adding the first (15.42593 eV) [5] and second (16.2494 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the hydrogen atom (13.59844 eV) [6] and the bond energy of  $H_2^*$  (2.651 eV) [7].

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The predicted  $D_3^+$  molecular bond dissociation energy,  $E_D$ , given by the difference between the total energy of  $D_3^+$  (Eqs. (13.30) where p=1 and (13.48)) and the experimental total energy of  $D_2$  [9-10]<sup>2</sup> is

$$E_D = -31.76 \ eV - \left(-36.134300 \ eV\right)$$
  
= 4.374300 \ eV

5 The  $D_3^+$  bond dissociation energy,  $E_D$ , given by Eq. (13.35) where p=1 is

$$E_D = 3.88777 \ eV + 0.485556 \ eV$$
  
= 4.373331 eV (13.53)

The results of the determination of bond parameters of  $H_3^+$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and 10 calculated results is excellent.

#### HYDROXYL RADICAL (OH)

The water molecule can be solved by first considering the solution of the hydroxyl radical which is formed by the reaction of a hydrogen atom and an oxygen atom:

$$15 H + O \rightarrow OH (13.54)$$

The hydroxyl radical OH can be solved using the same principles as those used to solve the hydrogen molecule wherein the diatomic molecular orbital (MO) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serves as basis function in linear combination with an oxygen atomic orbital (AO) to form the MO of OH.

- 20 The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of  $\hbar$ . A further constraint with the substitution of a heteroatom (0) for one of the hydrogen atoms is that the constant energy of the MO must
- 25 match the energy of the heteroatom.

<sup>&</sup>lt;sup>2</sup> The experimental total energy of the deuterium molecule is given by adding the first (15.466 eV) [9] and second (16.294 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the deuterium atom (13.603 eV) [10] and the bond energy of  $D_2^*$  (2.692 eV) [9].

#### FORCE BALANCE OF OH

OH comprises two spin-paired electrons in a chemical bond between the oxygen atom and the hydrogen atom such that one electron on O remains unpaired. The OH radical MO is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal H<sub>2</sub> MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the H-atom electron forms a H<sub>2</sub>-type ellipsoidal MO with one of the O-atom electrons. The O electron configuration given in the Eight-Electron Atoms section is 1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup>, and the orbital arrangement is

$$\begin{array}{cccc}
2p \text{ state} \\
\uparrow & \downarrow & \uparrow & \uparrow \\
\hline
1 & 0 & -1
\end{array}$$
(13.55)

10 corresponding to the ground state  ${}^{3}P_{2}$ .

In determining the central forces for O in the Radius and Ionization Energy of the Outer Electron of the Oxygen Atom section, it was shown that the energy is minimized with conservation of angular momentum by the cancellation of the orbital angular momentum of a  $p_x$  electron by that of the  $p_y$  electron with the pairing of electron eight to fill the  $p_x$  orbital. 15 Then, the diamagnetic force is given by Eq. (10.156) is that of atomic nitrogen (Eq. (10.136) corresponding to the  $p_z$ -orbital electron (Eq. (10.82) with m=0) as the source of diamagnetism with an additional contribution from the uncanceled  $p_x$  electron (Eq. (10.82) with m=1). From Eqs. (10.83) and (10.89), the paramagnetic force,  $\mathbf{F}_{mag 2}$ , is given by Eq. (10.157) corresponding to the spin-angular-momentum contribution alone of the  $p_x$  electron 20 and the orbital angular momentum of the  $p_z$  electron, respectively. The diamagnetic and paramagnetic forces cancel such that the central force is purely the Coulombic force. This central force is maintained with bond formation such that the energy of the O2p shell is unchanged. Thus, the angular momentum of each electron of the O2p shell is conserved with bond formation. The central paramagnetic force due to spin is provided by the spin-25 pairing force of the OH MO that has the symmetry of an s orbital that superimposes with the 2p orbitals such that the corresponding angular momenta of the O2p orbitals are unchanged.

The  $O2p_y$  electron combines with the H1s electron to form a molecular orbital. The proton of the H atom is along the internuclear axis. Due to symmetry, the other O electrons

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are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the OH MO involve only the  $O2p_y$  and H1s electrons and the change in the magnetic energy of the  $O2p_y$  electron with the other O electrons (Eq. (13.152)) with the formation of the OH MO. The forces are determined by these energies.

As in the case of  $H_2$ , the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into O atom for distances shorter than the radius of the 2p shell. Otherwise, the electric field of the other O2p electrons would be perturbed, and the 2p shell would not be stable. The corresponding increase in energy of O would not be offset by any energy decrease in the OH MO based on the distance from the O nucleus to the H1s electron compared to those of the O2p electrons. Thus, the MO surface comprises a prolate spheroid at the H proton that is continuous with the 2p shell at the O atom. The energy of the prolate spheroid is matched to that of the O2p shell.

The orbital energy E for each elliptical cross section of the prolate spheroidal MO is given by the sum of the kinetic T and potential V energies. E = T + V is constant, and the closed orbits are those for which  $T \triangleleft V \mid$ , and the open orbits are those for which  $T \trianglerighteq V \mid$ . It can be shown that the time average of the kinetic energy,  $\langle T \rangle$ , for elliptic motion in an inverse-squared field is 1/2 that of the time average of the magnitude of the potential energy,  $|\langle V \rangle|$ .  $|\langle T \rangle = 1/2 |\langle V \rangle|$  [11]. In the case of an atomic orbital (AO), E = T + V, and for all points on the AO, |E| = T = 1/2 |V|. As shown in the Hydrogen-type Molecular Ions section, each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptic plane cross section of the spheroidal MO through the foci. The motion is such that eccentric angle,  $\theta$ , changes at a constant rate at each point. That is  $\theta = \omega t$  at time t where  $\omega$  is a constant, and

25  $r(t) = \mathbf{i}a\cos\omega t + \mathbf{j}b\sin\omega t \tag{13.56}$ 

Consider the boundary condition that the MO of OH comprises a linear combination of an oxygen AO and a  $H_2$ -type ellipsoidal MO. The charge density of  $H_2$ -type ellipsoidal MO given by Eq. (13.4) maintains that the surface is an equipotential; however, the potential and kinetic energy of a point on the surface changes as it orbits the central field. The potential energy is a maximum and the kinetic energy is a minimum at the semimajor axis, and the reverse occurs at the semiminor axis. Since the time average of the kinetic energy, < T >, for

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elliptic motion in an inverse-squared field is 1/2 that of the time average of the magnitude of the potential energy, by symmetry, the < T >= 1/2 < |V| > condition holds for 1/2 of the  $H_2$ -type ellipsoidal MO having the H focus and ending at the plane defined by the semiminor axes. The O nucleus comprises the other focus of the OH MO. The O2p AO obeys the energy relationship for all points. Thus, the linear combination of the  $H_2$ -type ellipsoidal MO with the O2p AO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the O2p AO in order to match the energy relationships. Thus, the OH MO must comprise 75% of a  $H_2$ -type ellipsoidal MO (1/2 +25%) and an oxygen AO:

10 1 
$$O2p_{\nu} AO + 0.75 H_2 MO \rightarrow OH MO$$
 (13.57)

The force balance of the OH MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.57). The force constant k of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by 15 Eq. (11.65):

$$k = \frac{2e^2}{4\pi\varepsilon} \tag{13.58}$$

Since the  $H_2$ -type ellipsoidal MO comprises 75% of the OH MO, the electron charge density in Eq. (13.58) is given by -0.75e. Thus, k' of the  $H_2$ -type-ellipsoidal-MO component of the OH MO is

$$k' = \frac{(0.75)2e^2}{4\pi\varepsilon_0}$$
 (13.59)

L for the electron equals  $\hbar$ ; thus, the distance from the origin of the OH MO to each focus c' is given by Eqs. (11.79) and (13.59):

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 1.5a}} = \sqrt{\frac{2aa_0}{3}} \tag{13.60}$$

The internuclear distance from Eq. (13.60) is

$$2c' = 2\sqrt{\frac{2aa_0}{3}} \tag{13.61}$$

The length of the semiminor axis of the prolate spheroidal OH MO b=c given by Eq. (11.80) is

$$b = \sqrt{a^2 - c'^2} \tag{13.62}$$

The eccentricity, e, is

$$e = \frac{c'}{a} \tag{13.63}$$

Then, the solution of the semimajor axis a allows for the solution of the other axes of the 5 prolate spheroidal and eccentricity of the OH MO.

The general equation of the ellipsoidal MO having semiprincipal axes a, b, c given by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \tag{13.64}$$

is also completely determined by the total energy E given by Eq. (11.18):

10  $r = \frac{m\frac{L^2}{m^2}k^{-1}}{1 + \left(1 + 2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2}\cos\theta}$  (13.65)

The energy of the oxygen 2p shell is the negative of the ionization energy of the oxygen atom given by Eq. (10.163). Experimentally, the energy is [12]

$$E(2p \text{ shell}) = -E(\text{ionization}; O) = -13.6181 \text{ eV}$$
(13.66)

Since the prolate spheroidal MO transitions to the O AO, the energy E in Eq. (13.66) adds 15 to that of the  $H_2$ -type ellipsoidal MO to give the total energy of the OH MO. From the energy equation and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the OH MO are solved.

The energy components derived previously for the hydrogen molecule, Eqs. (11.207-11.212), apply in the case of the  $H_2$ -type ellipsoidal MO. As in the case of the energies of 20  $H_3^+(1/p)$  given by Eqs. (13.12-13.16), each energy component of the  $H_2$ -type ellipsoidal MO is the total for the two equivalent electrons with the exception that the total charge and energies of the two electrons is normalized by the percentage composition given by Eq. (13.57):

$$V_{e} = \left(\frac{3}{4}\right) \frac{-2e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}}$$
(13.67)

$$V_{p} = \frac{e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}}$$
 (13.68)

$$T = \left(\frac{3}{4}\right) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(13.69)

$$V_{m} = \left(\frac{3}{4}\right) \frac{-\hbar^{2}}{4m \cdot a\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}}$$
(13.70)

$$E_T = V_c + T + V_m + V_n ag{13.71}$$

$$E_T = -\frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \left[ \left( \frac{3}{2} - \frac{3}{4} \frac{a_0}{a} + \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right]$$
(13.72)

5 
$$E_{T} = -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right]$$
 (13.73)

Since the prolate spheroidal MO transitions to the O AO and the energy of the O2p shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.66), the total energy  $E_T(OH)$  of the OH MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the O AO and the  $H_2$ -type ellipsoidal MO that forms the OH MO as given by Eq. (13.57):

$$E_{T}(OH) = E_{T} + E(2p \text{ shell})$$

$$= E_{T} - E(\text{ionization}; O)$$

$$= -\frac{e^{2}}{8\pi\varepsilon_{0}c^{\prime}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a+c^{\prime}}{a-c^{\prime}} - 1 \right] - 13.6181 \text{ eV}$$
(13.74)

To match the boundary condition that the total energy of the entire the  $H_2$ -type ellipsoidal MO is given by Eq. (11.212):

$$E_T(H_2) = -\frac{e^2}{8\pi\epsilon_0 a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - \sqrt{2} \right] = -31.63536831 \, eV \quad (13.75)$$

15  $E_T(OH)$  given by Eq. (13.74) is set equal to Eq. (13.75):

$$E_{T}(OH) = -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 13.6181 \ eV = -31.63536831 \ eV$$
(13.76)

From the energy relationship given by Eq. (13.76) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the OH MO can be solved.

20 Substitution of Eq. (13.60) into Eq. (13.76) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1\right] = e18.01726831$$
(13.77)

The most convenient way to solve Eq. (13.77) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.26430a_0 = 6.69039 \ X \ 10^{-11} \ m \tag{13.78}$$

5 Substitution of Eq. (13.78) into Eq. (13.60) gives

$$c' = 0.91808a_0 = 4.85826 \ X \ 10^{-11} \ m \tag{13.79}$$

The internuclear distance given by multiplying Eq. (13.79) by two is

$$2c' = 1.83616a_0 = 9.71651 \times 10^{-11} m \tag{13.80}$$

The experimental bond distance is [13]

$$10 2c' = 9.71 \times 10^{-11} m (13.81)$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.62) gives

$$b = c = 0.86925a_0 = 4.59985 X 10^{-11} m ag{13.82}$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.63) gives

$$e = 0.72615 \tag{13.83}$$

The nucleus of the H atom and the nucleus of the O atom comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $O2p_y$  AO can be determined from the polar equation of the ellipse (Eq. (11.10)):

$$r = r_0 \frac{1+e}{1+e\cos\theta'} \tag{13.84}$$

20 The radius of the  $O2p_y$  AO given by Eq. (10.162) is  $r_8 = a_0$ , and the polar radial coordinate of the ellipse and the radius of the  $O2p_y$  AO are equal at the point of intersection. Thus, Eq. (13.84) becomes

$$a_0 = (a - c') \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a} \cos \theta'}$$
 (13.85)

such that the polar angle  $\theta'$  is given by

$$\theta' = \cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\frac{c'}{a}}{a_0}-1\right)\right)$$
 (13.86)

Substitution of Eqs. (13.78-13.79) into Eq. (13.86) gives

$$\theta' = 123.65^{\circ}$$
 (13.87)

Then, the angle  $\theta_{O2p_yAO}$  the radial vector of the  $O2p_y$  AO makes with the internuclear axis is

5 
$$\theta_{02p,A0} = 180^{\circ} - 123.65^{\circ} = 56.35^{\circ}$$
 (13.88)

as shown in Figure 7.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$  between the 10 internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the O radial vector obeys the following relationship:

$$a_0 \sin \theta_{O2p,AO} = b \sin \theta_{H,MO} \tag{13.89}$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{a_0 \sin 56.35^{\circ}}{b} \tag{13.90}$$

15 with the use of Eq. (13.88). Substitution of Eq. (13.82) into Eq. (13.90) gives

$$\theta_{H_2MO} = 73.27^{\circ}$$
 (13.91)

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.92}$$

20 Substitution of Eqs. (13.78) and (13.91) into Eq. (13.92) gives

$$d_{H_2MO} = 0.36397a_0 = 1.92606 X 10^{-11} m ag{13.93}$$

The distance  $d_{O2pAO}$  along the internuclear axis from the origin of the O atom to the point of intersection of the orbitals is given by

$$d_{O2pAO} = c' - d_{H_2MO} (13.94)$$

25 Substitution of Eqs. (13.79) and (13.93) into Eq. (13.94) gives

$$d_{O2pAO} = 0.55411a_0 = 2.93220 X 10^{-11} m ag{13.95}$$

119

As shown in Eq. (13.57), in addition to the p-orbital charge-density modulation, the uniform charge-density in the  $p_y$  orbital is increased by a factor of 0.25 and the H-atom density is decreased by a factor of 0.25. The internuclear axis of the O-H bond is perpendicular to the bonding  $p_y$  orbital. Using the orbital composition of OH (Eq. (13.57)), 5 the radii of  $O1s = 0.12739a_0$  (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = a_0$  (Eq. (10.162)) shells, and the parameters of the OH MO given by Eqs. (13.3-13.4), (13.78-13.80), (13.82-13.83), and (13.87-13.95), the dimensional diagram and charge-density of the OH MO comprising the linear combination of the  $H_2$ -type ellipsoidal MO and the O AO according to Eq. (13.57) are shown in Figures 7 and 8, respectively.

10

#### ENERGIES OF OH

The energies of OH given by the substitution of the semiprincipal axes (Eqs. (13.78-13.80) and (13.82)) into the energy equations (Eqs. (13.67-13.73)) are

$$V_e = \left(\frac{3}{4}\right) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -40.92709 \ eV$$
 (13.96)

15  $V_p = \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 14.81988 \ eV \tag{13.97}$ 

$$T = \left(\frac{3}{4}\right) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 16.18567 \, eV \tag{13.98}$$

$$V_{m} = \left(\frac{3}{4}\right) \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -8.09284 \ eV \tag{13.99}$$

$$E_T(OH) = -\frac{e^2}{8\pi\epsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 13.6181 \ eV = -31.63247 \ eV \ (13.100)$$

where  $E_T(OH)$  is given by Eq. (13.74) which is reiteratively matched to Eq. (13.75) within 20 five-significant-figure round-off error.

#### VIBRATION AND ROTATION OF OH

The vibrational energy of *OH* may be solved in the same manner as that of hydrogen-type molecular ions and hydrogen molecules given in the Vibration of Hydrogen-type Molecular 25 Ions section, and the Vibration of Hydrogen-type Molecules section, respectively, except that the orbital composition and the requirement that the *O2p* shell remain at the same energy and

radius in the OH MO as it is in the O atom must be considered. Each p-orbital comprises the sum of a constant function and a spherical harmonic function as given by Eq. (1.65). In addition to the p-orbital charge-density modulation, the uniform charge-density in  $p_{\gamma}$  orbital is increased by a factor of 0.25, and the H-atom electron density is decreased by a factor of 0.25. The force between the electron density of the  $H_2$ -type ellipsoidal MO and the nuclei determines the vibrational energy. With the radius of the orbit at the oxygen atom fixed at

$$r_8 = a_0 (13.101)$$

according to Eq. (10.162), the central-force terms for the reentrant orbit between the electron density and the nuclei of the  $H_2$ -type ellipsoidal MO are given by Eqs. (11.213-11.214), 10 except that the corresponding charge of -0.75e replaces the charge of -e of Eqs. (11.213-11.214). Furthermore, due to condition that the O2p shell remain at the same energy and radius in the OH MO as it is in the O atom, the oscillation of  $H_2$ -type ellipsoidal is along the semiminor axis with the apsidal angle of Eq. (11.140) given by  $\psi = \pi$ . Thus, the semimajor axis a of Eqs. (11.213-11.214) is replaced by the semiminor axis b:

15 
$$f(b) = -\frac{0.75e^2}{8\pi\varepsilon_0 b^2}$$
 (13.102)

and

$$f'(b) = \frac{0.75e^2}{4\pi\varepsilon_0 b^3}$$
 (13.103)

Here, the force factor of 0.75 is equal to the equivalent term of Eq. (13.59). As the  $H_2$ -type ellipsoidal oscillates along b, the internuclear distance changes 180° out of phase. Thus, the 20 distance for the reactive nuclear-repulsive terms is given by internuclear distance 2c' (Eq. (13.80)). Similar to that of Eqs. (11.215-11.216), the contribution from the repulsive force between the two nuclei is

$$f(2c') = \frac{e^2}{8\pi\varepsilon_0 (2c')^2}$$
 (13.104)

and

25 
$$f'(2c') = -\frac{e^2}{4\pi\varepsilon_0 (2c')^3}$$
 (13.105)

Thus, from Eqs. (11.136), (11.213-11.217), and (13.102-13.105), the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 b^3} - \frac{e^2}{8\pi\varepsilon_0 (2c')^3}}{\mu}}$$

$$= \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 (0.86925a_0)^3} - \frac{e^2}{8\pi\varepsilon_0 (1.83616a_0)^3}}{\frac{16}{17}m_p}}$$

$$= 6.96269 \times 10^{14} \ rad/s$$
(13.106)

where b is given by Eq. (13.82), 2c' is given by Eq. (13.80), and the reduced mass of  $^{16}OH$  is given by:

$$\mu_{^{16}OH} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1)(16)}{1 + 16} m_p \tag{13.107}$$

5 where  $m_p$  is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency,  $\omega(0)$ , for  $^{16}OH$  given by Eqs. (11.136), (11.148), and (13.106) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{763.18 \, Nm^{-1}}{\mu}} = 6.96269 \, X \, 10^{14} \, radians / s \tag{13.108}$$

where the reduced nuclear mass of  $^{16}OH$  is given by Eq.(13.107) and the spring constant, k(0), given by Eqs. (11.136) and (13.106) is

$$k(0) = 763.18 \ Nm^{-1}$$
 (13.109)

The  $^{16}OH$  transition-state vibrational energy,  $E_{vib}(0)$ , given by Planck's equation (Eq. (11.127)) is:

15 
$$E_{vib}(0) = \hbar\omega = \hbar 6.96269 X 10^{14} \ rad/s = 0.4583 \ eV = 3696.38 \ cm^{-1}$$
 (13.110)

Zero-order or zero-point vibration is not physical and is not observed experimentally as discussed in the Diatomic Molecular Vibration section; yet, there is a term  $\omega_e$  of the old point-particle-probability-wave-mechanics that can be compared to  $E_{vib}(0)$ . From Herzberg [14],  $\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{16}OH$  is

$$\omega_e = 3735.21 \ cm^{-1} \tag{13.111}$$

As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and

expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods. The energy  $\tilde{v}_{\nu}$  of state  $\nu$  is

5 
$$\tilde{v}_{n} = v\omega_{0} - v(v-1)\omega_{0}x_{0}, \quad v = 0,1,2,3...$$
 (13.112)

where

$$\omega_0 x_0 = \frac{hc\omega_0^2}{4D_0} \tag{13.113}$$

 $\omega_0$  is the frequency of the  $\upsilon=1 \rightarrow \upsilon=0$  transition, and  $D_0$  is the bond dissociation energy given by Eq. (13.162). From Eq. (13.112),  $\omega_0$  is given by

$$\omega_0 = E_{vib}(0) - 2\omega_0 x_0 \tag{13.114}$$

Substitution of Eq. (13.113) into Eq. (13.114) gives

$$\omega_0 = E_{vib}(0) - 2\frac{hc\omega_0^2}{4D_0} \tag{13.115}$$

Eq. (13.115) can be expressed as

$$\omega_0^2 + \frac{2D_0}{hc}\omega_0 - \frac{2D_0}{hc}E_{vib}(0) = 0 \tag{13.116}$$

15 which can be solved by the quadratic formula:

$$\omega_{0} = \frac{-\frac{2D_{0}}{hc} \pm \sqrt{\left(\frac{2D_{0}}{hc}\right)^{2} + 4\frac{2D_{0}}{hc}E_{vib}(0)}}{2}$$
(13.117)

Only the positive root is real, physical; thus,

$$\omega_0(cm^{-1}) = \frac{-\frac{2D_0}{100hc} + \sqrt{\left(\frac{2D_0}{100hc}\right)^2 + 4\frac{2D_0}{100hc}} E_{vib}(0)}{2}$$

$$= \frac{-\frac{2e(4.4104 \, eV)}{100hc} + \sqrt{\left(\frac{2e(4.4104 \, eV)}{100hc}\right)^2 + 4\frac{2e(4.4104 \, eV)}{100hc} \left(3696.37 \, cm^{-1}\right)}}{2}$$

$$= 3522.02 \, cm^{-1}$$

(13.118)

20

where  $E_{vib}(0)$  is given by Eq. (13.110) and  $D_0$  is given by Eq. (13.156). The corresponding  $^{16}OH$   $v=1 \rightarrow v=0$  vibrational energy,  $E_{vib}(1)$ , in electron volts is:

$$E_{vib}(1) = 0.43666 \ eV \tag{13.119}$$

The experimental vibrational energy of <sup>16</sup>OH is [16-17]

5 
$$E_{vib}(1) = 0.4424 \ eV$$
 (3568  $cm^{-1}$ ) (13.120)

Using Eqs. (13.118-13.119) with Eq. (13.113), the anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{16}OH$  is

$$\omega_0 x_0 = \frac{100hc \left( 8.06573X10^3 \frac{cm^{-1}}{eV} 0.43666 eV \right)^2}{4e \left( 4.4104 eV \right)} cm^{-1} = 87.18 cm^{-1}$$
 (13.121)

The experimental anharmonic perturbation term,  $\omega_0 x_0$ , of <sup>16</sup>OH [14] is

$$\omega_0 x_0 = 82.81 \ cm^{-1} \tag{13.122}$$

The vibrational energies of successive states are given by Eqs. (13.110), (13.112), and (13.121).

Using the reduced nuclear mass of <sup>16</sup>OD given by

$$\mu_{16_{OD}} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(16)}{2 + 16} m_p \tag{13.123}$$

15 where  $m_p$  is the proton mass, the corresponding parameters for deuterated hydroxyl radical  $^{16}OD$  (Eqs. (13.102-13.121) and (13.162)) are

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{763.18 \ Nm^{-1}}{\mu}} = 5.06610 \ X \ 10^{14} \ radians / s$$
 (13.124)

$$k(0) = 763.18 \, Nm^{-1} \tag{13.125}$$

$$E_{rib}(0) = \hbar\omega = \hbar 5.06610 X 10^{14} \ rad/s = 0.33346 \ eV = 2689.51 \ cm^{-1}$$
 (13.126)

$$\omega_{0}(cm^{-1}) = \frac{-\frac{2D_{0}}{100hc} + \sqrt{\left(\frac{2D_{0}}{100hc}\right)^{2} + 4\frac{2D_{0}}{100hc}E_{vib}(0)}}{2}$$

$$= \frac{-\frac{2e(4.4687 \ eV)}{100hc} + \sqrt{\left(\frac{2e(4.4687 \ eV)}{100hc}\right)^{2} + 4\frac{2e(4.4687 \ eV)}{100hc}(2689.51 \ cm^{-1})}}{2}$$

$$= 2596.02 \ cm^{-1}$$

(13.127)

$$E_{vib}(1) = 0.3219 \ eV$$
 (13.128)

$$\delta \omega_0 x_0 = \frac{100hc \left( 8.06573X10^3 \frac{cm^{-1}}{eV} 0.3219 eV \right)^2}{4e \left( 4.4687 eV \right)} cm^{-1} = 46.75 cm^{-1}$$
 (13.129)

From Herzberg [14],  $\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{16}OD$  is

$$\omega_e = 2720.9 \text{ cm}^{-1} \tag{13.130}$$

The experimental vibrational energy of <sup>16</sup>OD is [16-17]

10 
$$E_{vib}(1) = 0.3263 \ eV$$
 (2632.1 cm<sup>-1</sup>) (13.131)

and the experimental anharmonic perturbation term,  $\omega_0 x_0$ , of <sup>16</sup>OD [14] is

$$\omega_0 x_0 = 44.2 \ cm^{-1} \tag{13.132}$$

which match the predictions given by Eqs. (13.126), (13.127-13.128), and (13.129), respectively.

The  $B_e$  rotational parameters for  $^{16}OH$  and  $^{16}OD$  are given by Eq. (12.65):

$$B_e = \frac{\hbar^2}{2I_e hc} \tag{13.133}$$

where

$$I = \mu r^2 \tag{13.134}$$

Using the internuclear distance,  $r = 2c^{\dagger}$ , and reduced mass of  $^{16}OH$  given by Eqs. (13.80) and (13.107), respectively, the corresponding  $B_e$  is

$$B_e = 18.835 \ cm^{-1} \tag{13.135}$$

The experimental  $B_e$  rotational parameter of  $^{16}OH$  is [14]

$$B_s = 18.871 \text{ cm}^{-1} \tag{13.136}$$

Using the internuclear distance, r = 2c', and reduced mass of <sup>16</sup>OD given by Eqs. (13.80) and (13.123), respectively, the corresponding  $B_e$  is

$$B_{a} = 9.971 \text{ cm}^{-1} \tag{13.137}$$

5 The experimental  $B_a$  rotational parameter of  $^{16}OD$  is [14]

$$B_e = 10.01 \text{ cm}^{-1} \tag{13.138}$$

## THE DOPPLER ENERGY TERMS OF 16OH AND 16OD

The radiation reaction force in the case of the vibration of  $^{16}OH$  in the transition state 10 corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) and Eq. (13.22) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. Following the same consideration as those used to derive Eqs. (13.102-13.103) and Eqs. (11.231-11.232), the central force terms between the electron density and the nuclei of  $^{16}OH$  MO with the radius of the orbit at 15 the oxygen atom fixed at

$$r_8 = a_0 (13.139)$$

according to Eq. (10.162) are

$$f(b) = -\frac{0.75e^2}{4\pi\varepsilon_0 b^2} \tag{13.140}$$

and

20 
$$f'(b) = \frac{(0.75)2e^2}{4\pi\varepsilon_0 b^3}$$
 (13.141)

wherein the oscillation of  $H_2$ -type ellipsoidal MO is along the semiminor axis b with the apsidal angle of Eq. (11.140) given by  $\psi = \pi$  due to condition that the O2p shell remain at the same energy and radius in the OH MO as it is in the O atom. Thus, using Eqs. (11.136) and (13.140-13.141), the angular frequency of this oscillation is

25 
$$\omega = \sqrt{\frac{0.75e^2}{\frac{4\pi\varepsilon_0 b^3}{m_e}}} = 4.41776 \, X \, 10^{16} \, rad/s \tag{13.142}$$

The kinetic energy,  $E_{\kappa}$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 4.41776 \, X \, 10^{16} \, rad \, / \, s = 29.07844 \, eV$$
 (13.143)

In Eq. (11.181), substitution of the total energy of OH,  $E_T(OH)$ , (Eq. (13.76)) for  $E_{hv}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.143) for  $\overline{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit.

5 
$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(29.07844 \ eV)}{m_e c^2}} = -0.33749 \ eV$$
 (13.144)

The total energy of OH is decreased by  $\overline{E}_D$ .

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average 10 kinetic energy of vibration corresponding to the Doppler energy of the electrons,  $\overline{E}_{Kvib}$ , is 1/2 of the vibrational energy of OH given by Eq. (13.120). The decrease in the energy of the OH due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  and  $\overline{E}_{Kvib}$ . Using Eq. (13.144) and the experimental  $^{16}OH$   $\omega_e$  of 15 3735.21  $cm^{-1}$  (0.463111 eV) [16-17] gives

$$\overline{E}_{asc}(^{16}OH) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.145)

$$\overline{E}_{osc}(^{16}OH) = -0.33749 \ eV + \frac{1}{2}(0.463111 \ eV) = -0.10594 \ eV$$
 (13.146)

To the extent that the MO dimensions are the same, the electron reentrant orbital energies,  $\overline{E}_K$ , are the same independent of the isotope of hydrogen, but the vibrational 20 energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.144), Eqs. (13.145-13.146), and the experimental  $^{16}OD$   $\omega_e$  of 2720.9  $cm^{-1}$  (0.33735 eV) [16-17], the corresponding  $\overline{E}_{\alpha\kappa}(^{16}OD)$  is

$$\overline{E}_{osc}(^{16}OD) = -0.33749 \ eV + \frac{1}{2}(0.33735 \ eV) = -0.16881 \ eV$$
 (13.147)

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TOTAL AND BOND ENERGIES OF  $^{16}OH$  AND  $^{16}OD$  RADICALS  $E_{T+asc}(^{16}OH)$ , the total energy of the  $^{16}OH$  radical including the Doppler term, is given by the sum of  $E_{T}(OH)$  (Eq. (13.76)) and  $\overline{E}_{osc}(^{16}OH)$  given by Eqs. (13.142-13.146):

$$E_{T+osc}(^{16}OH) = V_s + T + V_m + V_p + E(2p \ shell) + \overline{E}_{osc}(^{16}OH)$$

$$= E_T(OH) + \overline{E}_{osc}(^{16}OH)$$
(13.148)

$$E_{T+osc}(^{16}OH) = \left\{ \frac{-e^2}{8\pi\varepsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 13.6181 \, eV \right\} \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{3}{4} \frac{e^2}{4\pi\varepsilon_0 b^3}}}{\frac{m_e}{m_e c^2}}} \right] + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

$$= -31.63537 \, eV - 0.33749 \, eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

$$(13.149)$$

From Eqs. (13.145-13.146) and (13.148-13.149), the total energy of  ${}^{16}OH$  is

$$E_{T+osc}(^{16}OH) = -31.63537 \ eV + \overline{E}_{osc}(^{16}OH)$$

$$= -31.63537 \ eV - 0.33749 \ eV + \frac{1}{2}(0.463111 \ eV)$$

$$= -31.74130 \ eV$$
(13.150)

where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.  $E_{T+osc}(^{16}OD)$ , the total energy of 10  $^{16}OD$  including the Doppler term, is given by the sum of  $E_T(OD) = E_T(OH)$  (Eq. (13.76)) and  $\overline{E}_{osc}(^{16}OD)$  given by Eq. (13.147):

$$E_{T+osc}(^{16}OD) = -31.63537 \ eV + \overline{E}_{osc}(^{16}OD)$$

$$= -31.63537 \ eV - 0.33749 \ eV + \frac{1}{2}(0.33735 \ eV)$$

$$= -31.80418 \ eV$$
(13.151)

where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term. The dissociation of the bond of the

hydroxyl radical forms a free hydrogen atom with one unpaired electron and an oxygen atom with two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101):

$$E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_o \mu_B^2}{a_0^3} = 0.114411 \ eV$$
 (13.152)

The corresponding bond dissociation energy,  $E_D$ , is given by the sum of the total energies of the oxygen atom and the corresponding hydrogen atom minus the sum of  $E_{T+ase}$  ( $^{16}OH$ ) and E(magnetic):

5 
$$E_D = E(^{16}O) + E(H) - E_{T+asc}(^{16}OH) - E(magnetic)$$
 (13.153)

 $E(^{16}O)$  is given by Eq. (13.66),  $E_D(H)$  [18] is

$$E(H) = -13.59844 \ eV \tag{13.154}$$

and  $E_D(D)$  [19] is

$$E(D) = -13.603 \ eV \tag{13.155}$$

10 The <sup>16</sup>OH bond dissociation energy,  $E_D(^{16}OH)$ , is given by Eqs. (13.150) and (13.152-13.155):

$$E_{D}(^{16}OH) = -(13.6181 \ eV + 13.59844 \ eV) - (E(magnetic) + E_{T+osc}(^{16}OH))$$

$$= -27.21654 \ eV - (0.114411 \ eV - 31.74130 \ eV)$$

$$= 4.4104 \ eV$$
(13.156)

The experimental <sup>16</sup>OH bond dissociation energy is [20]

$$E_D(^{16}OH) = 4.41174 \ eV \tag{13.157}$$

15 The <sup>16</sup>OD bond dissociation energy,  $E_D(^{16}OD)$ , is given by Eqs. (13.151-13.153):

$$E_{D}(^{16}OD) = -(13.6181 \ eV + 13.603 \ eV) - (E(magnetic) + E_{T+osc}(^{16}OD))$$

$$= -27.2211 \ eV - (0.114411 \ eV - 31.804183 \ eV)$$

$$= 4.4687 \ eV$$
(13.158)

The experimental  $^{16}OD$  bond dissociation energy is [21-22]

$$E_D(^{16}OD) = 4.454 \ eV$$
 (13.159)

The results of the determination of bond parameters of *OH* and *OD* are given in 20 Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

#### WATER MOLECULE $(H_2O)$

The water molecule  $H_2O$  is formed by the reaction of a hydrogen atom with a hydroxyl radical:

$$OH + H \rightarrow H_2O \tag{13.160}$$

5 The water molecule can be solved using the same principles as those used to solve the hydrogen molecule,  $H_3^+$ , and OH wherein the diatomic molecular orbital (MO) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serves as basis function in a linear combination with an oxygen atomic orbital (AO) to form the MO of  $H_2O$ . The solution is very similar to that of OH except that there are two OH bonds in water.

#### FORCE BALANCE OF $H_2O$

 $H_2O$  comprises two chemical bonds between oxygen and hydrogen. Each O-H bond comprises two spin-paired electrons with one from an initially unpaired electron of the oxygen atom and the other from the hydrogen atom. The  $H_2O$  MO is determined by considering properties of the binding atoms and the boundary constraints. The  $H_2$  prolate spheroidal MO satisfies the boundary constraints as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section; thus, each H-atom electron forms a  $H_2$ -type ellipsoidal MO with one of the initially unpaired O-atom electrons. The initial O electron configuration given in the Eight-Electron Atoms section is  $1s^2 2s^2 2p^4$ , and the orbital arrangement is given by Eqs. (10.154) and Eq. (13.55).

As shown in the case of OH in the Force Balance of OH section, the forces that determine the radius and the energy of the O2p shell are unchanged with bond formation. Thus, the angular momentum of each electron of the O2p is conserved with bond formation.

25 The central paramagnetic force due to spin of each O-H bond is provided by the spin-paring force of the  $H_2O$  MO that has the symmetry of an s orbital that superimposes with the O2p orbitals such that the corresponding angular momenta are unchanged.

Each of the  $O2p_z$  and  $O2p_x$  electron combines with a H1s electron to form a molecular orbital. The proton of the H atom is along the internuclear axis. Due to 30 symmetry, the other O electrons are equivalent to point charges at the origin. (See Eqs. (19-

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38) of Appendix IV.) Thus, the energies in the  $H_2O$  MO involve only each O2p and each H1s electron with the formation of each O-H bond. The forces are determined by these energies.

As in the case of  $H_2$ , each of two O-H-bond MOs is a prolate spheroid with the 5 exception that the ellipsoidal MO surface cannot extend into the O atom for distances shorter than the radius of the 2p shell. Otherwise, the electric field of the other O2p electrons would be perturbed, and the 2p shell would not be stable. The corresponding increase in energy of O would not be offset by any energy decrease in the O-H-bond MO based on the distance from the O nucleus to the H1s electron compared to those of the O2p electrons. Thus, the MO surface comprises a prolate spheroid at each H proton that is continuous with the 2p shell at the O atom. The sum of the energies of the prolate spheroids is matched to that of the 2p shell.

The orbital energy E for each elliptical cross section of the prolate spheroidal MO is given by the sum of the kinetic T and potential V energies. E = T + V is constant, and the closed orbits are those for which  $T \triangleleft V \mid$ , and the open orbits are those for which  $T \trianglerighteq \mid V \mid$ . It can be shown that the time average of the kinetic energy,  $\langle T \rangle$ , for elliptic motion in an inverse-squared field is 1/2 that of the time average of the magnitude of the potential energy,  $|\langle V \rangle|$ .  $|\langle T \rangle| = 1/2 |\langle V \rangle|$  [11]. In the case of an atomic orbital (AO), E = T + V, and for all points on the AO, |E| = T = 1/2 |V|. As shown in the Hydrogen-type Molecular Ions section, each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptic plane cross section of the spheroidal MO through the foci. The motion is such that eccentric angle,  $\theta$ , changes at a constant rate at each point. That is  $\theta = \omega t$  at time t where  $\omega$  is a constant, and

25  $r(t) = \mathbf{i}a\cos\omega t + \mathbf{j}b\sin\omega t \tag{13.161}$ 

Consider the boundary condition that the MO of  $H_2O$  comprises a linear combination of an oxygen AO and two  $H_2$ -type ellipsoidal MOs, one for each O-H-bond. The charge density of each  $H_2$ -type ellipsoidal MO given by Eqs. (11.44-11.45) and (13.3-13.4) maintains that the surface is an equipotential; however, the potential and kinetic energy of a point on the surface changes as it orbits the central field. The potential energy is a maximum and the kinetic energy is a minimum at the semimajor axis, and the reverse occurs at the semiminor

axis. Since the time average of the kinetic energy,  $\langle T \rangle$ , for elliptic motion in an inverse-squared field is 1/2 that of the time average of the magnitude of the potential energy, by symmetry, the  $\langle T \rangle = 1/2 \langle |V| \rangle$  condition holds for 1/2 of each  $H_2$ -type ellipsoidal MO having the H focus and ending at the plane defined by the semiminor axes. The O nucleus comprises the other focus of each OH-MO component of the  $H_2O$  MO. The O2p AO obeys the energy relationship for all points. Thus, the linear combination of the  $H_2$ -type ellipsoidal MO with the O2p AO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the O2p AO in order to match the energy relationships. Thus, the  $H_2O$  MO must comprise two O-H-bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO (1/2 +25%) and an oxygen AO:

$$[1 O2 p_z AO + 0.75 H_2 MO] + [1 O2 p_y AO + 0.75 H_2 MO] \rightarrow H_2O MO$$
 (13.162)

The force balance of the  $H_2O$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.162). The force constant k of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by Eq. (11.65):

$$k = \frac{2e^2}{4\pi\varepsilon_a} \tag{13.163}$$

Since the each  $H_2$ -type ellipsoidal MO comprises 75% of the O-H-bond MO, the electron charge density in Eq. (13.163) is given by -0.75e. Thus, k' of the each  $H_2$ -type-ellipsoidal-20 MO component of the  $H_2O$  MO is

$$k' = \frac{(0.75)2e^2}{4\pi\varepsilon_o} \tag{13.164}$$

L for the electron equals  $\hbar$ ; thus, the distance from the origin of each O-H-bond MO to each focus c' is given by Eqs. (11.79) and (13.164):

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 1.5a}} = \sqrt{\frac{2aa_0}{3}}$$
 (13.165)

25 The internuclear distance from Eq. (13.165) is

$$2c' = 2\sqrt{\frac{2aa_0}{3}} \tag{13.166}$$

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The length of the semiminor axis of the prolate spheroidal O-H-bond MO b=c given by Eq. (11.80) is

$$b = \sqrt{a^2 - c'^2} \tag{13.167}$$

The eccentricity, e, is

$$5 e = \frac{c'}{a} (13.168)$$

The solution of the semimajor axis a then allows for the solution of the other axes of the prolate spheroid and eccentricity of the O-H-bond MO.

The general equation of the ellipsoidal MO having semiprincipal axes a, b, c given by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \tag{13.169}$$

is also completely determined by the total energy E given by Eq. (11.18):

$$r = \frac{m\frac{L^2}{m^2}k^{-1}}{1 + \left(1 + 2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2}\cos\theta}$$
(13.170)

The energy of the oxygen 2p shell is the negative of the ionization energy of the oxygen atom given by Eqs. (10.163) and (13.66). Experimentally, the energy is [12]

15 
$$E(2p \text{ shell}) = -E(\text{ionization}; O) = -13.6181 \text{ eV}$$
 (13.171)

Since each of the two prolate spheroidal O-H-bond MOs comprises a  $H_2$ -type-ellipsoidal MO that transitions to the O AO, the energy E in Eq. (13.171) adds to that of the two corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $H_2O$  MO. From the energy equation and the relationship between the axes given by Eqs. (13.165-13.168), the 20 dimensions of the  $H_2O$  MO are solved.

The energy components defined previously for the molecule, Eqs. (11.207-11.212), apply in the case of  $H_2O$ . Since the  $H_2O$  MO comprises two equivalent O-H -bond MOs, each a linear combination of a  $H_2$ -type-ellipsoidal MO and an O2p AO, the corresponding energy component of the  $H_2O$  MO is given by the linear superposition of the component energies. Thus, the energy scale factor is given as two times the force factor, the term in parentheses in Eq. (13.164). In addition to the equivalence and linearity principles, this factor also arises from the consideration of the nature of each bond and the linear combination that

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forms the  $H_2O$  MO. Each O-H-bond-energy component is the total for the two equivalent electrons with the exception that the total charge of the two electrons is normalized over the three basis set functions, two O-H-bond MOs (OH-type ellipsoidal MOs given in the Energies of OH section) and one O2p AO. Thus, the contribution of the O-H-bond MOs to the  $H_2O$  MO energies are those given for  $H_2(1/p)$  in the Energies of Hydrogen-Type Molecules multiplied by a factor of 3/2 as in the case with  $H_3^+$  (Eqs. (13.12), (13.15), 13.18-13.20)). In addition, the two sets of equivalent nuclear-point-charge pairs give rise to a factor of two times the proton-proton repulsion energy given by Eq. (11.208). Thus, the component energies of the  $H_2O$  MO are twice the corresponding energies of the OH MO given by Eqs. (13.67-13.73). The parameters a, b, and c' are given by Eqs. (13.165-13.167), respectively.

$$V_e = 2\left(\frac{3}{4}\right) \frac{-2e^2}{8\pi\epsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = \left(\frac{3}{2}\right) \frac{-2e^2}{8\pi\epsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(13.172)

$$V_p = 2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2 - b^2}}\tag{13.173}$$

$$T = 2\left(\frac{3}{4}\right) \frac{\hbar^2}{2m \cdot a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = \left(\frac{3}{2}\right) \frac{\hbar^2}{2m \cdot a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(13.174)

$$V_{m} = 2\left(\frac{3}{4}\right) \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = \left(\frac{3}{2}\right) \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} (13.175)$$

15

$$E_T = V_e + T + V_m + V_p ag{13.176}$$

$$E_{T} = -\frac{e^{2}}{4\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} \left[ \left( \frac{3}{2} - \frac{3}{4} \frac{a_{0}}{a} + \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right]$$
(13.177)

$$E_{T} = -\frac{e^{2}}{4\pi\varepsilon_{0}c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right]$$
 (13.178)

Since the each prolate spheroidal  $H_2$ -type MO transitions to the O AO and the energy of the O AO and the energy of the 20 O2p shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.171), the total energy  $E_T(H_2O)$  of the  $H_2O$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the O AO and the two  $H_2$ -type ellipsoidal MOs that forms the  $H_2O$  MO as given by Eq. (13.162):

$$E_{T}(H_{2}O) = E_{T} + E(2p \text{ shell})$$

$$= E_{T} - E(\text{ionization}; O)$$

$$= -\frac{e^{2}}{4\pi\varepsilon_{0}c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 13.6181 \text{ eV}$$

$$(13.179)$$

The two hydrogen atoms and the oxygen atom can achieve an energy minimum as a linear combination of two  $H_2$ -type ellipsoidal MOs each having the proton and the oxygen nucleus as the foci. Each O-H-bond MO comprises the same O2p shell of constant energy given 5 by Eq. (13.171). Thus, the energy of the  $H_2O$  MO is also given by the sum of that of the two  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant oxygen atom of the linear combination given by Eq. (13.171):

$$E_{T}(2H_{2}-O) = -2\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] - E(2p \text{ shell})$$

$$= 2(-31.63536831 \text{ eV}) - (-13.6181 \text{ eV})$$

$$= -49.652637 \text{ eV}$$
(13.180)

 $E_T(H_2O)$  given by Eq. (13.179) is set equal to two times the energy of the  $H_2$ -type 10 ellipsoidal MO minus the energy of the O2p shell given by Eq. (13.180):

$$E_T(H_2O) = -\frac{e^2}{4\pi\varepsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 13.6181 \ eV = -49.652637 \ eV$$
(13.181)

From the energy relationship given by Eq. (13.181) and the relationship between the axes given by Eqs. (13.165-13.167), the dimensions of the  $H_2O$  MO can be solved.

15 Substitution of Eq. (13.165) into Eq. (13.181) gives

$$\frac{e^2}{4\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1\right] = e36.034537\tag{13.182}$$

The most convenient way to solve Eq. (13.182) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.2641a_0 = 6.68933 \ X \ 10^{-11} \ m \tag{13.183}$$

20 Substitution of Eq. (13.183) into Eq. (13.165) gives

$$c' = 0.918005a_0 = 4.85787 X 10^{-11} m ag{13.184}$$

The internuclear distance given by multiplying Eq. (13.184) by two is

$$2c' = 1.83601a_0 = 9.71574 \times 10^{-11} m \tag{13.185}$$

The experimental bond distance is [23]

$$2c' = 9.70 \pm .005 \ X \ 10^{-11} \ m$$
 (13.186)

Substitution of Eqs. (13.177-13.176) into Eq. (13.167) gives

$$b = c = 0.869031a_0 = 4.59871 \times 10^{-11} m$$
 (13.187)

Substitution of Eqs. (13.177-13.176) into Eq. (13.168) gives

$$e = 0.726212 \tag{13.188}$$

The nucleus of the H atom and the nucleus of the O atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the  $O2p_y$  AO or  $O2p_z$  AO can be determined from the polar equation of the ellipse (Eq. (11.10)):

$$r = r_0 \frac{1+e}{1+e\cos\theta'} \tag{13.189}$$

The radius of the O2p shell given by Eq. (10.162) is  $r_8 = a_0$ , and the polar radial coordinate of the ellipse and the radius of the O2p shell are equal at the point of intersection. Thus, Eq. 15 (13.189) becomes

$$a_0 = (a - c') \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a} \cos \theta'}$$
 (13.190)

such that the polar angle  $\theta'$  is given by

$$\theta' = \cos^{-1} \left( \frac{a}{c'} \left( (a - c') \frac{1 + \frac{c'}{a}}{a_0} - 1 \right) \right)$$
 (13.191)

Substitution of Eqs. (13.177-13.176) into Eq. (13.191) gives

$$\theta' = 123.66^{\circ} \tag{13.192}$$

Then, the angle  $\theta_{O2p4O}$  the radial vector of the O2p AO makes with the internuclear axis is

$$\theta_{O2pAO} = 180^{\circ} - 123.66^{\circ} = 56.33^{\circ}$$
 (13.193)

as shown in Figure 7. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$ 

25 between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the O radial vector obeys the following relationship:

$$a_0 \sin \theta_{O2pAO} = b \sin \theta_{H_2MO} \tag{13.194}$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{a_0 \sin \theta_{O2pAO}}{b} = \sin^{-1} \frac{a_0 \sin 56.33^{\circ}}{b}$$
 (13.195)

with the use of Eq. (13.193). Substitution of Eq. (13.188) into Eq. (13.195) gives

$$\theta_{H_2MO} = 73.28^{\circ} \tag{13.196}$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.197}$$

Substitution of Eqs. (13.183) and (13.196) into Eq. (13.197) gives

$$d_{H_2MO} = 0.3637a_0 = 1.9244 \ X \ 10^{-11} \ m \tag{13.198}$$

The distance  $d_{O2pAO}$  along the internuclear axis from the origin of the O atom to the point of intersection of the orbitals is given by

$$d_{O2pAO} = c' - d_{H,MO} ag{13.199}$$

Substitution of Eqs. (13.184) and (13.198) into Eq. (13.199) gives

$$d_{O2pAO} = 0.5543a_0 = 2.93343 \ X \ 10^{-11} \ m \tag{13.200}$$

In addition to the intersection of the  $H_2$ -type MO with the O2p shell, two adjoining ellipsoidal  $H_2$ -type MOs intersect at points of equipotential. The angle and distance parameters are given by Eqs. (13.595-13.600) for the limiting methane case wherein four adjoining intersecting  $H_2$ -type MOs have the possibility of forming a self-contained two-20 dimension equipotential surface of charge and current. Charge continuity can be obeyed for the  $H_2O$  MO if the current is continuous between the adjoining  $H_2$ -type MOs. However, in the limiting case of methane, the existence of a separate linear combination of the  $H_2$ -type MOs comprising four-spin paired electrons, not connected to the bonding carbon heteroatom requires that the electron be divisible. It is possible for an electron to form time-dependent singular points or nodes having no charge as shown by Eqs. (1.65a-1.65b), and two-dimensional charge distributions having Laplacian potentials and one-dimensional regions of zero charge are possible for macroscopic charge densities and currents as given in Haus and Melcher [24]. However, it is not possible for single electrons to have two dimensional discontinuities in charge based on internal forces and first principles discussed in Appendix

IV. Thus, at the points of intersection of the H<sub>2</sub>-type MOs of methane, symmetry, electron indivisibility, current continuity, and conservation of energy and angular momentum require that the current between the points of mutual contact and the carbon atom be projected onto and flow along the radial vector to the surface of the C2sp³ shell. This current designed the
5 bisector current (BC) meets the C2sp³ surface and does not travel to distances shorter than its radius. The methane result must also apply in the case of other bonds including that of the water molecule. Here, the H<sub>2</sub>-type MOs intersect and the ellipsoidal current is projected onto the radial vector to the O2p shell and does not travel to distances shorter than its radius as in the case of a single O-H bond.

As shown in Eq. (13.162), in addition to the p-orbital charge-density modulation, the uniform charge-density in the  $p_z$  and  $p_y$  orbitals is increased by a factor of 0.25 and the H atoms are each decreased by a factor of 0.25. Using the orbital composition of  $H_2O$  (Eq. (13.162)), the radii of  $Ols = 0.12739a_0$  (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = a_0$  (Eq. (10.162)) shells, and the parameters of the  $H_2O$  MO given by Eqs. (13.3-13.4), (13.183-13.185), (13.187-13.188), and (13.192-13.200), the charge-density of the  $H_2O$  MO comprising the linear combination of two O-H-bond MOs (OH-type ellipsoidal MOs given in the Energies of OH section) according to Eq. (13.162) is shown in Figure 9. Each O-H-bond MO comprises a  $H_2$ -type ellipsoidal MO and an O2p AO having the dimensional diagram shown in Figure 8.

20

## ENERGIES OF H,O

The energies of  $H_2O$  given by the substitution of the semiprincipal axes (Eqs. (13.183-13.185) and (13.187)) into the energy equations (Eqs. (13.172-13.180)) are

$$V_e = \left(\frac{3}{2}\right) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -81.8715 \ eV \tag{13.201}$$

25 
$$V_p = 2 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 29.6421 \, eV$$
 (13.202)

$$T = \left(\frac{3}{2}\right) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 32.3833 \ eV$$
 (13.203)

$$V_{m} = \left(\frac{3}{2}\right) \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -16.1917 \ eV$$
 (13.204)

$$E_T(H_2O) = -\frac{e^2}{4\pi\varepsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 13.6181 \ eV = -49.6558 \ eV \quad (13.205)$$

where  $E_T(H_2O)$  is given by Eq. (13.179) which is reiteratively matched to Eq. (13.180) within five-significant-figure round-off error.

# VIBRATION OF H,O

5

The vibrational energy levels of  $H_2O$  may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as 10 given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

#### THE DOPPLER ENERGY TERM OF H,O

The radiation reaction force in the case of the vibration of  $H_2O$  in the transition state corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) and Eqs. (13.22) and (13.144) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. As in the case of  $H_3^+$ , the water molecule is a linear combination of three orbitals. The water MO comprises two  $H_2$ -type ellipsoidal MOs and the O AO. Thus, the force factor of water in the determination of the Doppler frequency is equivalent to that of the  $H_3^+$  ion given in Eqs. (13.18-13.20) and given by Eq. (13.164). From Eqs. (11.231-11.232) and (13.18-13.20), the central force terms between the electron density and the nuclei of each O-H-bond MO with the radius of the orbit at the oxygen atom fixed at

$$r_8 = a_0 {(13.206)}$$

25 according to Eq. (10.162) with the oscillation along the semiminor axis are

$$f(b) = -\left(\frac{3}{2}\right) \frac{e^2}{4\pi\varepsilon_0 b^2}$$
 (13.207)

and

$$f'(b) = \left(\frac{3}{2}\right) \frac{2e^2}{4\pi\varepsilon_0 b^3} \tag{13.208}$$

Thus, using Eqs. (11.136) and (13.207-13.208), the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_a}} = 6.24996 \, X \, 10^{16} \, rad \, / s \tag{13.209}$$

The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

5 
$$\overline{E}_K = \hbar \omega = \hbar 6.24996 \, X \, 10^{16} \, rad / s = 41.138334 \, eV$$
 (13.210)

The three basis elements of water, H, H, and O, all have the same Coulombic energy as given by Eqs. (1.243) and (10.163), respectively, such that the Doppler energy involves the total energy of the  $H_2O$  MO. Thus, in Eq. (11.181), substitution of the total energy of  $H_2O$ ,  $E_T(H_2O)$ , (Eqs. (13.179-13.180) and Eq. (13.181)) for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.210) for  $\overline{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{hv} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -49.652637 \ eV \sqrt{\frac{2e(41.138334 \ eV)}{m_e c^2}} = -0.630041 \ eV \qquad (13.211)$$

The total energy of  $H_2O$  is decreased by  $\overline{E}_D$ .

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons,  $\overline{E}_{Kvib}$ , is 1/2 of the vibrational energy of  $H_2O$ . The decrease in the energy of  $H_2O$  due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{asc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  and  $\overline{E}_{Kvib}$ . Using Eq. (13.211) and the experimental  $H^{16}OH$  vibrational energy of  $E_{vib} = 3755.93 \ cm^{-1} = 0.465680 \ eV$  [25] gives

$$\overline{E}'_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.212)

$$\overline{E}'_{asc} = -0.630041 \ eV + \frac{1}{2} (0.465680 \ eV) = -0.397201 \ eV$$
 (13.213)

per bond. As in the case for  $H_3^+(1/p)$  shown in the Doppler Energy Term of  $H_3^+$ -type Molecular Ions section, the reentrant orbit for the binding of a hydrogen atom to a hydroxyl radical causes the bonds to oscillate by increasing and decreasing in length along the two O-H bonds at a relative phase angle of 180°. Since the vibration and reentrant oscillation 5 is along two bonds for the asymmetrical stretch  $(v_3)$ ,  $\overline{E}_{osc}$  for  $H^{16}OH$ ,  $\overline{E}_{osc}(H^{16}OH)$ , is:

$$\overline{E}_{osc}(H^{16}OH) = 2\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$= 2\left(-0.630041 \ eV + \frac{1}{2}(0.465680 \ eV)\right)$$

$$= -0.794402 \ eV$$
(13.214)

To the extent that the MO dimensions are the same, the electron reentrant orbital energies,  $\overline{E}_K$ , are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.211), Eqs. (13.212-13.214), and the experimental  $D^{16}OD$  vibrational energy of  $E_{vib} = 2787.92 \ cm^{-1} = 0.345661 \ eV$  [25], the corresponding  $\overline{E}_{osc}(D^{16}OD)$  is

$$\overline{E}_{osc}(D^{16}OD) = 2\left(-0.630041 \ eV + \frac{1}{2}(0.345661 \ eV)\right) 
= -0.914421 \ eV$$
(13.215)

#### 15 TOTAL AND BOND ENERGIES OF H<sup>16</sup>OH AND D<sup>16</sup>OD

 $E_{T+osc}(H_2^{16}O)$ , the total energy of the  $H^{16}OH$  including the Doppler term, is given by the sum of  $E_T(H_2O)$  (Eq. (13.181)) and  $\overline{E}_{osc}(H^{16}OH)$  given Eqs. (13.207-13.214):

$$E_{T+osc}(H_2^{16}O) = V_e + T + V_m + V_p + E(O2p) + \overline{E}_{osc}(H^{16}OH)$$

$$= E_T(H_2O) + \overline{E}_{osc}(H^{16}OH)$$
(13.216)

$$E_{T+osc}(H_2^{16}O) = \begin{cases} \left(\frac{-e^2}{4\pi\varepsilon_0 c'} \left(\left(\frac{3}{2} - \frac{3}{8} \frac{a_0}{a}\right) \ln \frac{a+c'}{a-c'} - 1\right) - 13.6181 \, eV\right) \left(1 + 2\sqrt{\frac{2\hbar\sqrt{\frac{3}{2} \frac{e^2}{4\pi\varepsilon_0 b^3}}{\frac{m_e}{m_e}c^2}}}\right) \\ + 2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \\ = -49.652637 \, eV - 2\left(0.630041 \, eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{cases}$$

$$(13.217)$$

From Eqs. (13.214) and (13.216-13.217), the total energy of  $H^{16}OH$  is

$$E_{T+osc}(H_2^{16}O) = -49.652637 \ eV + \overline{E}_{osc}(H^{16}OH)$$

$$= -49.652637 \ eV - 2\left(0.630041 \ eV - \frac{1}{2}(0.465680 \ eV)\right)$$

$$= -50.447039 \ eV$$
(13.218)

5 where the experimental vibrational energy was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.  $E_{T+ox}(D_2^{16}O)$ , the total energy of  $D^{16}OD$  including the Doppler term is given by the sum of  $E_T(D_2O) = E_T(H_2O)$  (Eq. (13.181)) and  $\overline{E}_{asc}(D^{16}OD)$  given by Eq. (13.215):

$$E_{T+osc}(D_2^{16}O) = -49.652637 \ eV + \overline{E}_{osc}(D^{16}OD)$$

$$= -49.652637 \ eV - 2\left(0.630041 \ eV - \frac{1}{2}(0.345661 \ eV)\right)$$

$$= -50.567058 \ eV$$
(13.219)

where the experimental vibrational energy was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term. As in the case of the

10 hydroxyl radical, the dissociation of the bond of the water molecule forms a free hydrogen atom and a hydroxyl radical, with one unpaired electron each. The lowering of the energy of the reactants due to the magnetic dipoles decreases the bond energy. Thus, the total energy of oxygen is reduced by the energy in the field of the two magnetic dipoles given by Eq. (13.152). The corresponding bond dissociation energy,  $E_D$ , is given by the sum of the total

energies of the corresponding hydroxyl radical and hydrogen atom minus the total energy of water,  $E_{T+osc}(H^{16}OH)$ , and E(magnetic).

Thus,  $E_D$  of  $H^{16}OH$  is given by:

$$E_{D}(H^{16}OH) = E(H) + E(^{16}OH) - E_{T+oso}(H^{16}OH) - E(magnetic)$$
 (13.220)

5 where  $E_T(^{16}OH)$  is given by the of the sum of the experimental energies of  $^{16}O$  (Eq. (13.171)), H (Eq. (13.154)), and the negative of the bond energy of  $^{16}OH$  (Eq. (13.157)):

$$E(^{16}OH) = -13.59844 \ eV - 13.6181 \ eV - 4.41174 \ eV = -31.62828 \ eV \tag{13.221}$$

From Eqs. (13.154), (13.218), and (13.220-13.221),  $E_D(H^{16}OH)$  is

$$\begin{split} E_D(H^{16}OH) &= E(H) + E(^{16}OH) - \left( E(magnetic) + E_{T+asc} \left( H^{16}OH \right) \right) \\ &= -13.59844 \ eV - 31.62828 \ eV - \left( 0.114411 \ eV - 50.447039 \ eV \right) \\ &= 5.1059 \ eV \end{split}$$

10 (13.222)

The experimental  $H^{16}OH$  bond dissociation energy is [26]

$$E_{\rm D}(H^{16}OH) = 5.0991 \ eV \tag{13.223}$$

Similarly,  $E_D$  of  $D^{16}OD$  is given by:

$$E_{D}(D^{16}OH) = E(D) + E(^{16}OD) - (E(magnetic) + E_{T+osc}(D^{16}OD))$$
 (13.224)

15 where  $E_T(^{16}OD)$  is given by the of the sum of the experimental energies of  $^{16}O$  (Eq. (13.171)), D (Eq. (13.155)), and the negative of the bond energy of  $^{16}OD$  (Eq. (13.159)):

$$E(^{16}OD) = -13.603 \ eV -13.6181 \ eV -4.454 \ eV = -31.6721 \ eV$$
 (13.225)

From Eqs. (13.155), (13.220), and (13.224-13.225),  $E_D(D^{16}OD)$  is

$$E_D(D^{16}OD) = -13.603 \ eV - 31.6721 \ eV - (0.114411 \ eV - 50.567058 \ eV)$$

$$= 5.178 \ eV$$
(13.226)

20 The experimental  $D^{16}OD$  bond dissociation energy is [27]

$$E_D(D^{16}OD) = 5.191 \text{ eV} {(13.227)}$$

## BOND ANGLE OF H<sub>2</sub>O

The  $H_2O$  MO comprises a linear combination of two O-H-bond MOs. Each O-H-bond 25 MO comprises the superposition of a  $H_2$ -type ellipsoidal MO and the  $O2p_z$  AO or the

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 $O2p_y$  AO with a relative charge-density of 0.75 to 1.25; otherwise, the O2p orbitals are the same as those of the oxygen atom. A bond is also possible between the two H atoms of the O-H bonds. Such H-H bonding would decrease the O-H-bond strength since electron density would be shifted from the O-H bonds to the H-H bond. Thus, the bond angle between the two O-H bonds is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal H atoms of the O-H bonds is zero. Since the two  $H_2$ -type ellipsoidal MOs comprise 75% of the H electron density of  $H_2$ ; the energies and the total energy  $E_T$  of the H-H bond is given by Eqs. (13.67-13.73). From Eq. (11.79), the distance from the origin to each focus of the H-H ellipsoidal MO is

10 
$$c' = a \sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}}$$
 (13.228)

The internuclear distance from Eq. (13.228) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{13.229}$$

The length of the semiminor axis of the prolate spheroidal H-H MO b=c is given by Eq. (13.167). Substitution of Eq. (13.228) into Eq. (13.73) gives

15 
$$E_{T} = -\frac{e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1 \right]$$
 (13.230)

The radiation reaction force in the case of the vibration of H-H in the transition state corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy  $E_T$  that includes the radiation reaction of the H-H MO is given by the sum of  $E_T$  (Eq. (13.73)) and  $\overline{E}_{asc}(H_2)$  given Eqs. 20 (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy  $E_T(H-H)$  of the H-H MO including the Doppler term is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc} (H - H)$$
 (13.231)

$$E_{T} = \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{4\pi\varepsilon_{0}a^{3}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{4\pi\varepsilon_{0}a^{3}}{m_{e}}}} \right] + \frac{1}{2}\hbar\sqrt{\frac{\hbar}{\mu}}$$

$$= \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{0.75e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{4\pi\varepsilon_{0}a^{3}}{m_{e}}}} \right] + \frac{1}{2}\hbar\sqrt{\frac{n_{0}}{2}} + \frac{1}{2}\hbar\sqrt{$$

To match the boundary condition that the total energy of the H-H ellipsoidal MO is zero,  $E_T(H-H)$  given by Eq. (13.232) is set equal to zero:

$$0 = \begin{bmatrix} -e^{2} \\ 8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}} & \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{0.75e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] \\ + \frac{1}{2}\hbar\sqrt{\frac{0.75e^{2}}{8\pi\varepsilon_{o}a^{3}} - \frac{e^{2}}{8\pi\varepsilon_{o}(a + c')^{3}}}{0.5m_{p}}$$

$$(13.233)$$

5 From the energy relationship given by Eq. (13.233) and the relationship between the axes given by Eqs. (13.165-13.167), the dimensions of the H-H MO can be solved.

The most convenient way to solve Eq. (13.233) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 4.300a_0 = 2.275 X 10^{-10} m ag{13.234}$$

10 Substitution of Eq. (13.234) into Eq. (13.228) gives

$$c' = 1.466a_0 = 7.759 \ X \ 10^{-11} \ m \tag{13.235}$$

The internuclear distance given by multiplying Eq. (13.235) by two is

$$2c' = 2.933a_0 = 1.552 X 10^{-10} m ag{13.236}$$

Substitution of Eqs. (13.234-13.235) into Eq. (13.167) gives

15 
$$b = c = 4.042a_0 = 2.139 \times 10^{-10} m$$
 (13.237)

Substitution of Eqs. (13.234-13.235) into Eq. (13.168) gives

$$e = 0.341 \tag{13.238}$$

Using, distance between the two H atoms when the total energy of the corresponding MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$A^2 + B^2 - 2AB \operatorname{cosine} \theta = C^2 \tag{13.239}$$

5 With  $A = B = 2c'_{O-H}$ , the internuclear distance of each O-H bond given by Eq. (13.185), and  $C = 2c'_{H-H}$ , the internuclear distance of the two H atoms, the bond angle between the O-H bonds is given by

$$(2c'_{O-H})^2 + (2c'_{O-H})^2 - 2(2c'_{O-H})^2 \cos in\theta = (2c'_{H-H})^2$$
(13.240)

$$\theta = \cos^{-1}\left(\frac{2(2c'_{O-H})^2 - (2c'_{H-H})^2}{2(2c'_{O-H})^2}\right)$$
(13.241)

10 Substitution of Eqs. (13.185) and (13.236) into Eq. (13.241) gives

$$\theta = \cos^{-1} \left( \frac{2(1.836)^2 - (2.933)^2}{2(1.836)^2} \right)$$

$$= \cos^{-1} (-0.2756)$$

$$= 105.998^{\circ}$$
(13.242)

The experimental internuclear distance of the two H atoms,  $2c'_{H-H}$ , is [23].

$$2c'_{H-H} = 1.55 \pm 0.01 \ X \ 10^{-10} \ m$$
 (13.243)

which matches Eq. (13.236) very well. The experimental angle between the O-H bonds is 15 [23]

$$\theta = 106^{\circ} \tag{13.244}$$

which matches the predicted angle given by Eq. (13.242).

The results of the determination of bond parameters of  $H_2O$  and  $D_2O$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, 20 exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

#### **HYDROGEN NITRIDE (NH)**

The ammonia molecule can be solved by first considering the solution of the hydrogen and 25 dihydrogen nitride radicals. The former is formed by the reaction of a hydrogen atom and a nitrogen atom:

$$H + N \to NH \tag{13.245}$$

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The hydrogen nitride radicals, NH and  $NH_2$ , and ammonia,  $NH_3$ , can be solved using the same principles as those used to solve OH and  $H_2O$ .

#### FORCE BALANCE OF NH

the orbital arrangement is

5 NH comprises two spin-paired electrons in a chemical bond between the nitrogen atom and the hydrogen atom such that two electrons on N remain unpaired. The NH radical molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal H<sub>2</sub> MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the H-atom electron forms a H<sub>2</sub>-type ellipsoidal MO with one of the N-atom electrons. The N electron configuration given in the Seven-Electron Atoms section is 1s<sup>2</sup>2s<sup>2</sup>2p<sup>3</sup>, and

corresponding to the ground state  ${}^4S^0_{3/2}$ . The  $N2p_x$  electron combines with the H1s electron to form a molecular orbital. The proton of the H atom is along the internuclear axis. Due to symmetry, the other N electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the NH MO involve only the  $N2p_x$  and H1s electrons and the change in the magnetic energy of the  $N2p_x$  electron with the other N electrons (Eq. (13.305)) with the formation of the NH MO. The forces are determined by these energies.

As in the case of  $H_2$ , the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into N atom for distances shorter than the radius of the 2p shell. Thus, the MO surface comprises a prolate spheroid at the H proton that is continuous with the 2p shell at the N atom whose nucleus serves as the other focus. The energy of the prolate spheroid is matched to that of the N2p shell. As in the case with OH, the linear combination of the  $H_2$ -type ellipsoidal MO with the N2p AO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the N2p atomic orbital (AO) in order to match potential, kinetic, and orbital energy relationships. Thus, the NH MO must comprise 75% of a  $H_2$ -type ellipsoidal MO and a nitrogen AO:

$$1 N2p_x AO + 0.75 H_2 MO \rightarrow NH MO$$
 (13.247)

The force balance of the NH MO is determined by the boundary conditions that arise from 5 the linear combination of orbitals according to Eq. (13.247) and the energy matching condition between the hydrogen and nitrogen components of the MO.

Similar to the OH case given by Eq. (13.59), the  $H_2$ -type ellipsoidal MO comprises 75% of the NH MO; so, the electron charge density in Eq. (11.65) is given by -0.75e. Based on the condition that the electron MO is an equipotential energy surface, Eq. (11.79) 10 gives the ellipsoidal parameter c' in terms of the central force of the foci, the electron angular momentum, and the ellipsoidal parameter a. To meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the N AO, the force constant used to determine the ellipsoidal parameter c' is normalized by the ratio of the ionization energy of N 14.53414 eV [6] and 13.605804 eV, the magnitude of the Coulombic energy between the 15 electron and proton of H given by Eq. (1.243). This normalizes the force to match that of the Coulombic force alone to met the force matching condition of the NH MO under the influence of the proton and the N nucleus. Thus, k' of Eq. (11.79) to determine c' is

$$k' = \frac{(0.75)2e^2}{4\pi\varepsilon_0 \frac{14.53414}{13.605804}} = (0.936127)\frac{(0.75)2e^2}{4\pi\varepsilon_0}$$
(13.248)

L for the electron equals  $\hbar$ ; thus, the distance from the origin of the NH MO to each focus 20 c' is given by Eqs. (11.79) and (13.248):

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 1.5a(0.936127)}} = \sqrt{\frac{2aa_0}{3(0.936127)}} = \sqrt{0.712154aa_0}$$
 (13.249)

The internuclear distance from Eq. (13.249) is

$$2c' = 2\sqrt{0.712154aa_0} \tag{13.250}$$

The length of the semiminor axis of the prolate spheroidal NH MO b=c is given by Eqs. 25 (11.80) and (13.62). The eccentricity, e, is given by Eq. (13.63). Then, the solution of the semimajor axis a allows for the solution of the other axes of the prolate spheroidal and eccentricity of the NH MO.

The energy of the nitrogen 2p shell is the negative of the ionization energy of the nitrogen atom given by Eq. (10.143). Experimentally, the energy is [6]

10 by Eq. (13.247):

$$E(2p \text{ shell}) = -E(\text{ionization}; N) = -14.53414 \text{ eV}$$
 (13.251)

Since the prolate spheroidal MO transitions to the N AO, the energy E in Eq. (13.251) adds to that of the  $H_2$ -type ellipsoidal MO to give the total energy of the NH MO. From the energy equation and the relationship between the axes given by Eqs. (13.249-13.250) and 5 (13.62-13.63), the dimensions of the NH MO are solved.

The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  are the same as those of OH given by Eqs. (13.67-13.73). Similarly to OH, the total energy  $E_T(NH)$  of the NH MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the N AO and the  $H_2$ -type ellipsoidal MO that forms the NH MO as given

$$E_{T}(NH) = E_{T} + E(2p \text{ shell})$$

$$= E_{T} - E(\text{ionization}; N)$$

$$= -\frac{e^{2}}{8\pi\epsilon_{c}c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV}$$
(13.252)

To match the boundary condition that the total energy of the entire the  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75),  $E_T(NH)$  given by Eq. (13.252) is set equal to Eq. (13.75):

15 
$$E_{T}(NH) = -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \ eV = -31.63536831 \ eV$$
(13.253)

From the energy relationship given by Eq. (13.252) and the relationship between the axes given by Eqs. (13.249-13.250) and (13.62-13.63), the dimensions of the *NH* MO can be solved.

20 Substitution of Eq. (13.249) into Eq. (13.253) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{0.712154aa_0}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{0.712154aa_0}}{a - \sqrt{0.712154aa_0}} - 1 \right] = e17.10123$$
 (13.254)

The most convenient way to solve Eq. (13.254) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.36275 a_0 = 7.21136 \ X \ 10^{-11} \ m \tag{13.255}$$

25 Substitution of Eq. (13.255) into Eq. (13.249) gives

$$c' = 0.98513a_0 = 5.21310 \ X \ 10^{-11} \ m \tag{13.256}$$

The internuclear distance given by multiplying Eq. (13.256) by two is

$$2c' = 1.97027a_0 = 1.04262 \times 10^{-10} m \tag{13.257}$$

The experimental bond distance is [28]

$$2c' = 1.0362 X 10^{-10} m ag{13.258}$$

5 Substitution of Eqs. (13.255-13.256) into Eq. (13.62) gives

$$b = c = 0.94159a_0 = 4.98270 X 10^{-11} m ag{13.259}$$

Substitution of Eqs. (13.255-13.256) into Eq. (13.63) gives

$$e = 0.72290 (13.260)$$

The nucleus of the H atom and the nucleus of the N atom comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $N2p_x$  AO are given by Eqs. (13.84-13.95). The polar intersection angle  $\theta'$  is given by

$$\theta' = \cos^{-1} \left( \frac{a}{c'} \left( (a - c') \frac{1 + \frac{c'}{a}}{r_n} - 1 \right) \right)$$
 (13.261)

where  $r_n = r_7 = 0.93084a_0$  is the radius of the N atom. Substitution of Eqs. (13.255-13.256)

15 into Eq. (13.86) gives

$$\theta' = 114.61^{\circ}$$
 (13.262)

Then, the angle  $\theta_{N2p_xAO}$  the radial vector of the  $N2p_x$  AO makes with the internuclear axis is

$$\theta_{N2p,AO} = 180^{\circ} - 114.61^{\circ} = 65.39^{\circ}$$
 (13.263)

as shown in Figure 10.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the N radial vector obeys the following relationship:

$$r_7 \sin \theta_{N2p_2AO} = 0.93084 a_0 \sin \theta_{N2p_2AO} = b \sin \theta_{H_2MO}$$
 (13.264)

25 such that

$$\theta_{H_2MO} = \sin^{-1} \frac{0.93084a_0 \sin \theta_{N2p_2AO}}{b} = \sin^{-1} \frac{0.93084a_0 \sin 65.39^{\circ}}{b}$$
(13.265)

with the use of Eq. (13.263). Substitution of Eq. (13.259) into Eq. (13.265) gives

$$\theta_{H_2MO} = 64.00^{\circ}$$
 (13.266)

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.267}$$

5 Substitution of Eqs. (13.255) and (13.266) into Eq. (13.267) gives

$$d_{H_2MO} = 0.59747a_0 = 3.16166 X 10^{-11} m ag{13.268}$$

The distance  $d_{N2pAO}$  along the internuclear axis from the origin of the N atom to the point of intersection of the orbitals is given by

$$d_{N2pAO} = c' - d_{H_2MO} (13.269)$$

10 Substitution of Eqs. (13.79) and (13.93) into Eq. (13.94) gives

$$d_{N2pAO} = 0.38767a_0 = 2.05144 X 10^{-11} m ag{13.270}$$

As shown in Eq. (13.247), in addition to the p-orbital charge-density modulation, the uniform charge-density in the  $p_x$  orbital is increased by a factor of 0.25 and the H-atom density is decreased by a factor of 0.25. The internuclear axis of the N-H bond is 15 perpendicular to the bonding  $p_x$  orbital. Using the orbital composition of NH (Eq. (13.27)), the radii of  $N1s = 0.14605a_0$  (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)), and  $N2p = 0.93084a_0$  (Eq. (10.142)) shells, and the parameters of the NH MO given by Eqs. (13.3-13.4) and (13.255-13.270), the dimensional diagram and charge-density of the NH MO comprising the linear combination of the  $H_2$ -type ellipsoidal MO and the N AO according to Eq. (13.247) are shown in Figures 10 and 11, respectively.

#### ENERGIES OF NH

The energies of NH given by the substitution of the semiprincipal axes (Eqs. (13.255-13.256) and (13.259)) into the energy equations (Eqs. (13.67-13.73)) are

25 
$$V_e = \left(\frac{3}{4}\right) \frac{-2e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -37.85748 \ eV \tag{13.271}$$

$$V_p = \frac{e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} = 13.81113 \ eV \tag{13.272}$$

$$T = \left(\frac{3}{4}\right) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 13.89011 \ eV$$
 (13.273)

$$V_{m} = \left(\frac{3}{4}\right) \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -6.94505 \ eV$$

$$E_{T}(NH) = -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ \left(\frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a}\right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \ eV = -31.63544 \ eV$$

$$(13.275)$$

where  $E_T(NH)$  is given by Eq. (13.253) which is reiteratively matched to Eq. (13.75) within 5 five-significant-figure round-off error.

## VIBRATION AND ROTATION OF NH

The vibrational energy of NH may be solved in the same manner as that of OH. From Eqs. (13.102-13.106) with the substitution of the NH parameters, the angular frequency of the 10 oscillation is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 b^3} - \frac{e^2}{8\pi\varepsilon_0 (2c')^3}}{\mu}}$$

$$= \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 (0.94159a_0)^3} - \frac{e^2}{8\pi\varepsilon_0 (1.97027a_0)^3}}{\frac{14}{15}m_p}}$$

$$= 6.18700 \times 10^{14} \text{ rad/s}$$
(13.276)

where b is given by Eq. (13.259), 2c' is given by Eq. (13.257), and the reduced mass of  $^{14}NH$  is given by:

$$\mu_{^{14}NH} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1)(14)}{1 + 14} m_p \tag{13.277}$$

where  $m_p$  is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency,  $\omega(0)$ , for <sup>14</sup>NH given by Eqs. (11.136), (11.148), and (13.276) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{597.59 \ Nm^{-1}}{\mu}} = 6.18700 \ X \ 10^{14} \ radians / s \tag{13.278}$$

20 where the reduced nuclear mass of  $^{14}NH$  is given by Eq.(13.277) and the spring constant, k(0), given by Eqs. (11.136) and (13.276) is

$$k(0) = 597.59 Nm^{-1}$$
 (13.279)

The <sup>14</sup>NH transition-state vibrational energy,  $E_{vib}(0)$ , given by Planck's equation (Eq. (11.127)) is:

$$E_{vib}(0) = \hbar\omega = \hbar 6.18700 X 10^{14} rad/s = 0.407239 eV = 3284.58 cm^{-1}$$
 (13.280)

5  $\omega_e$ , from the experimental curve fit of the vibrational energies of <sup>14</sup>NH is [28]

$$\omega_e = 3282.3 \text{ cm}^{-1} \tag{13.281}$$

Using Eqs. (13.112-13.118) with  $E_{vib}(0)$  given by Eq. (13.280) and  $D_0$  given by Eq. (13.311), the <sup>14</sup>NH  $v=1 \rightarrow v=0$  vibrational energy,  $E_{vib}(1)$  is

$$E_{vib}(1) = 0.38581 \ eV$$
 (3111.84 cm<sup>-1</sup>) (13.282)

10 The experimental vibrational energy of <sup>14</sup>NH using  $\omega_e$  and  $\omega_e x_e$  [28] according to K&P [15] is

$$E_{vib}(1) = 0.38752 \ eV \qquad (3125.5 \ cm^{-1}) \tag{13.283}$$

Using Eq. (13.113) with  $E_{vib}$  (1) given by Eq. (13.282) and  $D_0$  given by Eq. (13.311), the anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{14}NH$  is

$$\omega_0 x_0 = 86.37 \ cm^{-1} \tag{13.284}$$

The experimental anharmonic perturbation term,  $\omega_0 x_0$ , of <sup>14</sup>NH [28] is

$$\omega_0 x_0 = 78.4 \text{ cm}^{-1} \tag{13.285}$$

The vibrational energies of successive states are given by Eqs. (13.280), (13.112), and (13.284).

20 Using b given by Eq. (13.259), 2c' given by Eq. (13.257),  $D_0$  given by Eq. (13.314), and the reduced nuclear mass of  $^{14}ND$  given by

$$\mu_{\mathsf{M}_{ND}} = \frac{m_{\mathsf{I}} m_{\mathsf{2}}}{m_{\mathsf{1}} + m_{\mathsf{2}}} = \frac{(2)(14)}{2 + 14} m_{\mathsf{p}} \tag{13.286}$$

where  $m_p$  is the proton mass, the corresponding parameters for deuterium nitride <sup>14</sup>ND (Eqs. (13.102-13.121)) are

25 
$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{597.59 \text{ Nm}^{-1}}{\mu}} = 4.51835 \text{ X } 10^{14} \text{ radians/s}$$
 (13.287)

$$k(0) = 579.59 \ Nm^{-1} \tag{13.288}$$

$$E_{vib}(0) = \hbar\omega = \hbar 4.51835 X 10^{14} \ rad/s = 0.29741 \ eV = 2398.72 \ cm^{-1}$$
 (13.289)

$$E_{vib}(1) = 0.28710 \ eV$$
 (2305.35 cm<sup>-1</sup>) (13.290)

$$\omega_0 x_0 = 47.40 \ cm^{-1} \tag{13.291}$$

 $\omega_e$ , from the experimental curve fit of the vibrational energies of <sup>14</sup>ND is [28]

$$\delta \omega_{e} = 2398 \ cm^{-1} \tag{13.292}$$

The experimental vibrational energy of  $^{14}ND$  using  $\omega_e$  and  $\omega_e x_e$  [28] according to K&P [15] is

$$E_{vib}(1) = 0.2869 \ eV$$
 (2314 cm<sup>-1</sup>) (13.293)

and the experimental anharmonic perturbation term,  $\omega_0 x_0$ , of <sup>14</sup>ND [28] is

$$\omega_0 x_0 = 42 \text{ cm}^{-1} \tag{13.294}$$

which match the predictions given by Eqs. (13.289), (13.290) and (13.291), respectively.

Using Eqs. (13.133-13.134) and the internuclear distance, r = 2c', and reduced mass of <sup>14</sup>NH given by Eqs. (13.257) and (13.277), respectively, the corresponding  $B_e$  is

$$B_e = 16.495 \text{ cm}^{-1} \tag{13.295}$$

15 The experimental  $B_e$  rotational parameter of  $^{14}NH$  is [28]

$$B_{g} = 16.6993 \ cm^{-1} \tag{13.296}$$

Using the internuclear distance, r = 2c', and reduced mass of <sup>14</sup>ND given by Eqs. (13.257) and (13.286), respectively, the corresponding  $B_a$  is

$$B_e = 8.797 \ cm^{-1} \tag{13.297}$$

20 The experimental  $B_e$  rotational parameter of  $^{14}ND$  is [28]

$$B_e = 8.7913 \ cm^{-1} \tag{13.298}$$

## THE DOPPLER ENERGY TERMS OF 14NH AND 14ND

The equations of the radiation reaction force of hydrogen and deuterium nitride are the same as those of the corresponding hydroxyl radicals with the substitution of the hydrogen and deuterium nitride parameters. Using Eqs. (11.136) and (13.140-13.141), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}} = 3.91850 \, X \, 10^{16} \, rad/s \tag{13.299}$$

where b is given by Eq. (13.259). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar \omega = \hbar 3.91850 \, X \, 10^{16} \, rad \, / \, s = 25.79224 \, eV$$
 (13.300)

5 In Eq. (11.181), substitution of the total energy of NH,  $E_T(NH)$ , (Eq. (13.253)) for  $E_{hr}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.300) for  $\overline{E}_{\nu}$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(25.79224 \ eV)}{m_e c^2}} = -0.31785 \ eV \tag{13.301}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the 10 transition state at their corresponding frequency. The decrease in the energy of NH due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_{D}$  given by Eq. (13.301) and  $\bar{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of NH. Using the experimental  $^{14}NH$   $\omega_e$  of 3282.3 cm $^{-1}$  (0.40696 eV) [28]

15  $\overline{E}_{osc}(^{14}NH)$  is

$$\overline{E}_{osc} \left(^{14} NH\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}$$
(13.302)

$$\overline{E}_{osc}(^{14}NH) = -0.31785 \ eV + \frac{1}{2}(0.40696 \ eV) = -0.11437 \ eV$$
 (13.303)

Using Eqs. (13.301) and the experimental  $^{14}ND$   $\omega_e$  of 2398  $cm^{-1}$  (0.29732 eV) [28]  $\overline{E}_{osc}(^{14}ND)$  is

20 
$$\overline{E}_{osc}(^{14}ND) = -0.31785 \ eV + \frac{1}{2}(0.29732 \ eV) = -0.16919 \ eV$$
 (13.304)

### TOTAL AND BOND ENERGIES OF "NH AND "ND

 $E_{T+asc}(NH)$ , the total energy of the <sup>14</sup>NH radical including the Doppler term, is given by the sum of  $E_T(NH)$  (Eq. (13.253)) and  $\overline{E}_{osc}(^{14}NH)$  given by Eq. (13.303):

$$E_{T+osc}(NH) = V_e + T + V_m + V_p + E(2p \text{ shell}) + \overline{E}_{osc}(^{14}NH)$$

$$= E_T(NH) + \overline{E}_{osc}(^{14}NH)$$
(13.305)

$$E_{T+osc}(NH) = \left\{ \frac{-e^2}{8\pi\varepsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \ eV \right\} \left[ 1 + \sqrt{\frac{\frac{3}{4} \frac{e^2}{4\pi\varepsilon_0 b^3}}{\frac{m_e}{m_e}}} \right] + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}$$

$$= -31.63537 \ eV - 0.31785 \ eV + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}$$

$$(13.306)$$

From Eqs. (13.302-13.303) and (13.305-13.306), the total energy of  $^{14}NH$  is

$$E_{T+osc}(NH) = -31.63537 \ eV + \overline{E}_{osc}(^{14}NH)$$

$$= -31.63537 \ eV - 0.31785 \ eV + \frac{1}{2}(0.40696 \ eV)$$

$$= -31.74974 \ eV$$
(13.307)

where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.  $E_{T+asc}(ND)$ , the total energy of  $^{14}ND$  including the Doppler term, is given by the sum of  $E_T(ND) = E_T(NH)$  (Eq. (13.253)) and  $\overline{E}_{osc}(^{14}ND)$  given by Eq. (13.304):

$$E_{T+osc}(ND) = -31.63537 \ eV + \overline{E}_{osc}(^{14}ND)$$

$$= -31.63537 \ eV - 0.31785 \ eV + \frac{1}{2}(0.29732 \ eV)$$

$$= -31.80456 \ eV$$
(13.308)

where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term. The dissociation of the bond of the hydrogen nitride forms a free hydrogen atom with one unpaired electron and a nitrogen atom with three unpaired electrons as shown in Eq. (13.246). The  $p_x$  and  $p_y$  fields cancel and the magnetic energy (Eq. (7.46) with  $r_7 = 0.93084a_0$  is subtracted due to the one component of  $E_{mag}$  given by Eq. (10.137):

15 
$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 \left(0.93084a_0\right)^3} = \frac{8\pi\mu_0 \mu_B^2}{\left(0.93084a_0\right)^3} = 0.14185 \ eV$$
 (13.309)

The corresponding bond dissociation energy,  $E_D$ , is given by the sum of the total energies of the nitrogen atom and the corresponding hydrogen atom minus the sum of  $E_{T+asc}(NH)$  and E(magnetic):

$$E_{D} = E(^{14}N) + E(H) - E_{T+asc}(NH) - E(magnetic)$$
 (13.310)

5  $E(^{14}N)$  is given by Eq. (13.251),  $E_D(H)$  is given by Eq. (13.154), and  $E_D(D)$  is given by Eq. (13.155). The  $^{14}NH$  bond dissociation energy,  $E_D(^{14}NH)$ , is given by Eqs. (13.154), (13.251), (13.307), and (13.309-13.310):

$$E_{D}(^{14}NH) = -(14.53414 \ eV + 13.59844 \ eV) - (E(magnetic) + E_{T+ose}(NH))$$

$$= -28.13258 \ eV - (0.14185 - 31.74974 \ eV)$$

$$= 3.47530 \ eV$$
(13.311)

The experimental <sup>14</sup>NH bond dissociation energy from Ref. [29] and Ref. [30] is

$$E_D(^{14}NH) = 3.42 \ eV \tag{13.312}$$

$$E_D(^{14}NH) \le 3.47 \ eV \tag{13.313}$$

The <sup>14</sup>ND bond dissociation energy,  $E_D(^{14}ND)$ , is given by Eqs. (13.155), (13.251), (13.308), and (13.309-13.310):

$$E_{D}(^{14}ND) = -(14.53414 \ eV + 13.603 \ eV) - (E(magnetic) + E_{T+ose}(ND))$$

$$= -28.13714 \ eV - (0.14185 - 31.80456 \ eV)$$

$$= 3.5256 \ eV$$
(13.314)

15 The experimental <sup>14</sup>ND bond dissociation energy from Ref. [31] and Ref. [30] is

$$E_{D_{pos}}(^{14}ND) \le 339 \ kJ/mol = 3.513 \ eV$$
 (13.315)

$$E_{D}(^{14}ND) \le 3.54 \ eV \tag{13.316}$$

The results of the determination of bond parameters of NH and ND are given in Table 13.1. The calculated results are based on first principles and given in closed-form, 20 exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## DIHYDROGEN NITRIDE (NH2)

The dihydrogen nitride radical  $NH_2$  is formed by the reaction of a hydrogen atom with a 25 hydrogen nitride radical:

$$NH + H \rightarrow NH_2 \tag{13.317}$$

 $NH_2$  can be solved using the same principles as those used to solve  $H_2O$ . Two diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with two nitrogen atomic orbitals (AOs) to form the MO of  $NH_2$ . The solution is very similar to that of NH except that there are two NH bonds in  $NH_2$ .

#### FORCE BALANCE OF NH2

NH<sub>2</sub> comprises two chemical bonds between nitrogen and hydrogen. Each N-H bond comprises two spin-paired electrons with one from an initially unpaired electron of the nitrogen atom and the other from the hydrogen atom. Each H-atom electron forms a H<sub>2</sub>-type ellipsoidal MO with one of the initially unpaired N-atom electrons, 2p<sub>x</sub> or 2p<sub>y</sub>, such that the proton and the N nucleus serve as the foci. The initial N electron configuration given in the Seven-Electron Atoms section is 1s<sup>2</sup>2s<sup>2</sup>2p<sup>3</sup>, and the orbital arrangement is given by Eqs. (10.134) and (13.246). The radius and the energy of the N2p shell are unchanged with bond formation. The central paramagnetic force due to spin of each N-H bond is provided by the spin-pairing force of the NH<sub>2</sub> MO that has the symmetry of an s orbital that superimposes with the N2p orbitals such that the corresponding angular momenta are unchanged.

As in the case of  $H_2$ , each of two N-H-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into N atom for distances shorter than the radius of the 2p shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at each H proton that is continuous with the 2p shell at the N atom. The energies in the  $NH_2$  MO involve only each N2p and each H1s electron with the formation of each N-H bond. The sum of the energies of the prolate spheroids is matched to that of the 2p shell. The forces are determined by these energies. As in the case of NH, the linear combination of each  $H_2$ -type ellipsoidal MO with each N2p AO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the N2p AO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $NH_2$  MO must comprise two

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N-H bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO (1/2 +25%) and a nitrogen AO:

$$[1 N2p_x AO + 0.75 H_2 MO] + [1 N2p_y AO + 0.75 H_2 MO] \rightarrow NH_2 MO$$
 (13.318)

5

The force constant k' of the each  $H_2$ -type-ellipsoidal-MO component of the  $NH_2$  MO is given by Eq. (13.248). The distance from the origin of each N-H-bond MO to each focus c' is given by Eq. (13.249). The internuclear distance is given by Eq. (13.250). The length of the semiminor axis of the prolate spheroidal N-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each N-H-bond MO. Since each of the two prolate spheroidal N-H-bond MOs comprises a  $H_2$ -type-ellipsoidal MO that transitions to the N-AO, the energy E in Eq. (13.251) adds to that of the two corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $NH_2$ -MO. From the energy equation and the relationship between the axes, the dimensions of the  $NH_2$ -MO are solved.

The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  are twice those of OH and NH given by Eqs. (13.67-13.73) and equal to those of  $H_2O$  given by Eqs. (13.172-13.178). Similarly to  $H_2O$ , since the each prolate spheroidal  $H_2$ -type MO transitions to the N AO and the energy of the N2p shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.251), the total energy  $E_T(NH_2)$  of the  $NH_2$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the N AO and the two  $H_2$ -type ellipsoidal MOs that forms the  $NH_2$  MO as given by Eq. (13.318):

$$E_{T}(NH_{2}) = E_{T} + E(2p \text{ shell})$$

$$= E_{T} - E(\text{ionization}; N)$$

$$= -\frac{e^{2}}{4\pi\varepsilon_{0}c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV}$$
(13.319)

The two hydrogen atoms and the nitrogen atom can achieve an energy minimum as a linear combination of two  $H_2$ -type ellipsoidal MOs each having the proton and the nitrogen nucleus as the foci. Each N-H-bond MO comprises the same N2p shell of constant

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energy given by Eq. (13.251). Thus, the energy of the  $NH_2$  MO is also given by the sum of that of the two  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant nitrogen atom of the linear combination given by Eq. (13.251):

$$E_{T}(2H_{2}-N) = -2\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] - E(2p \text{ shell})$$

$$= 2\left( -31.63536831 \text{ eV} \right) - \left( -14.53414 \text{ eV} \right)$$

$$= -48.73660 \text{ eV}$$
(13.320)

5  $E_T(NH_2)$  given by Eq. (13.319) is set equal to two times the energy of the  $H_2$ -type ellipsoidal MO minus the energy of the N2p shell given by Eq. (13.320):

$$E_T(NH_2) = -\frac{e^2}{4\pi\varepsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.53414 \ eV = -48.73660 \ eV$$
(13.321)

From the energy relationship given by Eq. (13.321) and the relationship between the axes 10 given by Eqs. (13.248-13.250) and (13.62-13.63), the dimensions of the NH<sub>2</sub> MO can be solved.

Substitution of Eq. (13.249) into Eq. (13.321) gives

$$\frac{e^2}{4\pi\varepsilon_0\sqrt{0.712154aa_0}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{0.712154aa_0}}{a - \sqrt{0.712154aa_0}} - 1 \right] = e^{34.20246}$$
 (13.322)

The most convenient way to solve Eq. (13.322) is by the reiterative technique using a 15 computer. The result to within the round-off error with five-significant figures is

$$a = 1.36276a_0 = 7.21141 \ X \ 10^{-11} \ m \tag{13.323}$$

Substitution of Eq. (13.323) into Eq. (13.249) gives

$$c' = 0.98514a_0 = 5.21312 X 10^{-11} m ag{13.324}$$

The internuclear distance given by multiplying Eq. (13.324) by two is

$$2c' = 1.97027a_0 = 1.04262 X 10^{-10} m ag{13.325}$$

The experimental bond distance is [32]

$$2c' = 1.024 X 10^{-10} m ag{13.326}$$

Substitution of Eqs. (13.323-13.324) into Eq. (13.62) gives

$$b = c = 0.94160a_0 = 4.98276 X 10^{-11} m ag{13.327}$$

25 Substitution of Eqs. (13.323-13.324) into Eq. (13.63) gives

$$e = 0.72290 \tag{13.328}$$

The nucleus of the H atom and the nucleus of the N atom comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the  $N2p_x$  AO or  $N2p_y$  AO are given by Eqs. (13.84-13.95) and (13.261-13.270). Using Eqs. (13.323-13.325) and (13.327-13.328), the polar intersection angle  $\theta'$  given by Eq. (13.261) with  $r_n = r_7 = 0.93084a_0$  is

$$\theta' = 114.61^{\circ}$$
 (13.329)

Then, the angle  $\theta_{N2pAO}$  the radial vector of the  $N2p_x$  AO or  $N2p_y$  AO makes with the internuclear axis is

$$\theta_{N2pAO} = 180^{\circ} - 114.61^{\circ} = 65.39^{\circ} \tag{13.330}$$

10 as shown in Figure 10. The angle  $\theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the N radial vector given by Eqs. (13.264-13.265), (13.327), and (13.330) is

$$\theta_{H_2MO} = 64.00^{\circ}$$
 (13.331)

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.267), (13.323), and (13.331) is

$$d_{H_{\gamma MO}} = 0.59748a_0 = 3.16175 X 10^{-11} m ag{13.332}$$

The distance  $d_{N2pAO}$  along the internuclear axis from the origin of the N atom to the point of intersection of the orbitals given by Eqs. (13.269), (13.324), and (13.332) is

$$d_{N2pAO} = 0.38765 a_0 = 2.05137 X 10^{-11} m$$
 (13.333)

As shown in Eq. (13.318), in addition to the p-orbital charge-density modulation, the uniform charge-density in the  $p_x$  and  $p_y$  orbitals is increased by a factor of 0.25 and the H atoms are each decreased by a factor of 0.25. Using the orbital composition of  $NH_2$  (Eq. (13.318)), the radii of  $N1s = 0.14605a_0$  (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)), and 25  $N2p = 0.93084a_0$  (Eq. (10.142)) shells, and the parameters of the  $NH_2$  MO given by Eqs. (13.3-13.4) and (13.323-13.333), the charge-density of the  $NH_2$  MO comprising the linear combination of two N-H-bond MOs (NH-type ellipsoidal MOs given in the Energies of NH section) according to Eq. (13.318) is shown in Figure 12. Each N-H-bond MO

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comprises a  $H_2$ -type ellipsoidal MO and an N2p AO having the dimensional diagram shown in Figure 10.

#### ENERGIES OF NH,

5 The energies of  $NH_2$  given by the substitution of the semiprincipal axes ((Eqs. (13.323-13.325) and (13.327)) into the energy equations (Eqs. (13.172-13.176)) are

$$V_e = \left(\frac{3}{2}\right) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -75.71422 \ eV \tag{13.334}$$

$$V_p = 2\frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 27.62216 \, eV \tag{13.335}$$

$$T = \left(\frac{3}{2}\right) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 27.77974 \ eV$$
 (13.336)

10 
$$V_{m} = \left(\frac{3}{2}\right) \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -13.88987 \ eV$$
 (13.337)

$$E_T(NH_2) = -\frac{e^2}{4\pi\varepsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.53414 \ eV = -48.73633 \ eV$$
(13.338)

where  $E_T(NH_2)$  is given by Eq. (13.319) which is reiteratively matched to Eq. (13.320) within five-significant-figure round-off error.

15

#### VIBRATION OF NH,

The vibrational energy levels of  $NH_2$  may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as 20 given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

# THE DOPPLER ENERGY TERM OF NH<sub>2</sub>

The radiation reaction force in the case of the vibration of  $NH_2$  in the transition state 25 corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) and Eqs. (13.22) and (13.144)

that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. The equations of the radiation reaction force of dihydrogen and dideuterium nitride are the same as those of the corresponding water molecules with the substitution of the dihydrogen and dideuterium nitride parameters. Using Eqs. (11.136) and (13.207-13.209), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 5.54150 \, X \, 10^{16} \, rad/s \tag{13.339}$$

where b is given by Eq. (13.327). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

10 
$$\overline{E}_K = \hbar \omega = \hbar 5.54150 \, X \, 10^{16} \, rad / s = 36.47512 \, eV$$
 (13.340)

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.340) for  $\overline{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

15 
$$\overline{E}_D \cong E_{hv} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(36.47512 \ eV)}{m_e c^2}} = -0.37798 \ eV$$
 (13.341)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $NH_2$  due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (13.341) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of  $NH_2$ . Using the experimental  $^{14}NH_2$  vibrational energy of  $E_{vib} = 3301.110 \ cm^{-1} = 0.40929 \ eV$  [33] gives

$$\overline{E}'_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.342)

$$\overline{E}'_{osc} = -0.37798 \ eV + \frac{1}{2} (0.40929 \ eV) = -0.17334 \ eV$$
 (13.343)

25 per bond. As in the case for  $H_2O$ , the reentrant orbit for the binding of a hydrogen atom to a NH radical causes the bonds to oscillate by increasing and decreasing in length along the

two N-H bonds at a relative phase angle of 180°. Since the vibration and reentrant oscillation is along two bonds for the asymmetrical stretch  $(v_3)$ ,  $\overline{E}_{osc}$  for  $^{14}NH_2$ ,  $\overline{E}_{osc}(^{14}NH_2)$ , is:

$$\overline{E}_{osc} \left( {}^{14}NH_2 \right) = 2 \left( \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) 
= 2 \left( -0.37798 \, eV + \frac{1}{2} \left( 0.40929 \, eV \right) \right) 
= -0.34668 \, eV$$
(13.344)

Using Eq. (13.341), Eqs. (13.342-13.344), and the  $^{14}ND_2$  vibrational energy of  $E_{vib} = 2410.79 \ cm^{-1} = 0.29890 \ eV$ , calculated from the experimental  $^{14}NH_2$  vibrational energy using Eq. (11.148), the corresponding  $\overline{E}_{osc} \left(^{14}ND_2\right)$  is

$$\overline{E}_{osc} (^{14}ND_2) = 2 \left( -0.37798 \ eV + \frac{1}{2} (0.29890 \ eV) \right) 
= -0.45707 \ eV$$
(13.345)

## 10 TOTAL AND BOND ENERGIES OF "NH2 AND "ND2

 $E_{T+asc}\left(^{14}NH_{2}\right)$ , the total energy of the  $^{14}NH_{2}$  including the Doppler term, is given by the sum of  $E_{T}\left(NH_{2}\right)$  (Eq. (13.321)) and  $\overline{E}_{asc}\left(^{14}NH_{2}\right)$  given Eqs. (13.339-13.344):

$$E_{T+asc}(^{14}NH_{2}) = V_{e} + T + V_{m} + V_{p} + E(N2p) + \overline{E}_{asc}(^{14}NH_{2})$$

$$= E_{T}(NH_{2}) + \overline{E}_{asc}(^{14}NH_{2})$$
(13.346)

$$E_{T+osc}(^{14}NH_{2}) = \begin{cases} \left(\frac{-e^{2}}{4\pi\varepsilon_{0}c'}\left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] - 14.53414 \,eV\right) \\ \left(-2\left(31.63536831 \,eV\right)\sqrt{\frac{\frac{3}{2}\frac{e^{2}}{4\pi\varepsilon_{0}b^{3}}}{\frac{m_{e}}{m_{e}c^{2}}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}}\right) \end{cases}$$

$$= -48.73660 \,eV - 2\left(0.37798 \,eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$(13.347)$$

15 From Eqs. (13.344) and (13.346-13.347), the total energy of  $^{14}NH_2$  is

$$E_{T+osc} {14NH_2} = -48.73660 \ eV + \overline{E}_{osc} {14NH_2}$$

$$= -48.73660 \ eV - 2 \left( 0.37798 \ eV - \frac{1}{2} (0.40929 \ eV) \right)$$

$$= -49.08328 \ eV$$
(13.348)

where the experimental  $^{14}NH_2$  vibrational energy was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.  $E_{T+acc}(^{14}ND_2)$ , the total energy of  $^{14}ND_2$  including the Doppler term is given by the sum of  $E_T(ND_2) = E_T(NH_2)$  (Eq. (13.321)) and  $\overline{E}_{osc}(^{14}ND_2)$  given by Eq. (13.345):

$$E_{T+osc}(^{14}ND_2) = -48.73660 \ eV + \overline{E}_{osc}(^{14}ND_2)$$

$$= -48.73660 \ eV - 2\left(0.37798 \ eV - \frac{1}{2}(0.29890 \ eV)\right)$$

$$= -49.19366 \ eV$$
(13.349)

where the experimental  ${}^{14}NH_2$  vibrational energy corrected for the reduced mass difference of hydrogen and deuterium was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term. The corresponding bond dissociation energy,  $E_D$ , is given by the sum of the total energies of the corresponding hydrogen nitride radical and hydrogen atom minus the total energy of dihydrogen nitride,  $E_{T+osc}({}^{14}NH_2)$ .

Thus,  $E_D$  of  $^{14}NH_2$  is given by:

5

$$E_{D}(^{14}NH_{2}) = E(H) + E(^{14}NH) - E_{T+osc}(^{14}NH_{2})$$
(13.350)

where  $E_T(^{14}NH)$  is given by the of the sum of the experimental energies of  $^{14}N$  (Eq. (13.251)), H (Eq. (13.154)), and the negative of the bond energy of  $^{14}NH$  (Eq. (13.312)):

15 
$$E(^{14}NH) = -13.59844 \ eV - 14.53414 \ eV - 3.42 \ eV = -31.55258 \ eV$$
 (13.351)

From Eqs. (13.154), (13.348), and (13.350-13.351),  $E_D(^{14}NH_2)$  is

$$E_{D}(^{14}NH_{2}) = E(H) + E(^{14}NH) - E_{T+osc}(^{14}NH_{2})$$

$$= -13.59844 \ eV - 31.55258 \ eV - (-49.08328 \ eV)$$

$$= 3.9323 \ eV$$
(13.352)

The experimental  $^{14}NH_2$  bond dissociation energy from Ref. [34] and Ref. [35] is

$$E_D(^{14}NH_2) = 88 \pm 4 \ kcal / mole = 3.8160 \ eV$$
 (13.353)

$$E_D(^{14}NH_2) = 91.0 \pm 0.5 \ kcal \ / \ mole = 3.9461 \ eV$$
 (13.354)

Similarly,  $E_D$  of <sup>14</sup> $ND_2$  is given by:

$$E_{D}(^{14}ND_{2}) = E(D) + E(^{14}ND) - (E_{T+asc}(^{14}ND_{2}))$$
(13.355)

where  $E_r(^{14}ND)$  is given by the of the sum of the experimental energies of  $^{14}N$  (Eq. 5 (13.251)), D (Eq. (13.155)), and the negative of the bond energy of  $^{14}ND$  (Eq. (13.315)):

$$E(^{14}ND) = -13.603 \ eV - 14.53414 \ eV - 3.513 \ eV = -31.6506 \ eV \tag{13.356}$$

From Eqs. (13.155), (13.349), and (13.355-13.356),  $E_D(^{14}ND_2)$  is

$$E_D(^{14}ND_2) = -13.603 \ eV - 31.6506 \ eV - (-49.19366 \ eV)$$

$$= 3.9401 \ eV$$
(13.357)

The  $^{14}ND_2$  bond dissociation energy calculated from the average of the experimental bond 10 energies [34-35] and vibrational energy of  $^{14}NH_2$  [33] is

$$E_D(^{14}ND_2) = E_D(^{14}NH_2) + \frac{1}{2} \left( E_{vlb} (^{14}NH_2) - E_{vlb} (^{14}ND_2) \right)$$

$$= \frac{1}{2} \left( 3.8160 \ eV + 3.9461 \ eV \right) + \frac{1}{2} \left( 0.40929 \ eV - 0.29890 \ eV \right)$$

$$= 3.9362 \ eV$$
(13.358)

### BOND ANGLE OF NH,

The  $NH_2$  MO comprises a linear combination of two N-H-bond MOs. Each N-H-bond 15 MO comprises the superposition of a  $H_2$ -type ellipsoidal MO and the  $N2p_x$  AO or the  $N2p_y$  AO with a relative charge density of 0.75 to 1.25; otherwise, the N2p AOs are the same as those of the nitrogen atom. A bond is also possible between the two H atoms of the N-H bonds. Such H-H bonding would decrease the N-H bond strength since electron density would be shifted from the N-H bonds to the H-H bond. Thus, the bond 20 angle between the two N-H bonds is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal H atoms of the N-H bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the H-H ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_o}{2}}$$
 (13.359)

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{13.360}$$

The length of the semiminor axis of the prolate spheroidal H-H MO b=c is given by Eq. (13.167).

Since the two  $H_2$ -type ellipsoidal MOs comprise 75% of the H electron density of  $H_2$  and the energy of each  $H_2$ -type ellipsoidal MO is matched to that of the N2p AO; the component energies and the total energy  $E_T$  of the H-H bond are given by Eqs. (13.67-13.73) except that  $V_e$ , T, and  $V_m$  are corrected for the energy matching factor of 0.93613 given in Eq. (13.248). Substitution of Eq. (13.359) into Eq. (13.233) with the energy-

$$0 = \begin{bmatrix} \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left[ (0.93613)^{-1} \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_o a^3}}}{\frac{m_e}{m_e}c^2}} \right] \\ + \frac{1}{2}\hbar\sqrt{\frac{0.75e^2}{8\pi\varepsilon_o a^3} \frac{e^2}{8\pi\varepsilon_o (a + c')^3}}{0.5m_p}$$

$$(13.361)$$

From the energy relationship given by Eq. (13.361) and the relationship between the axes given by Eqs. (13.359-13.360) and (13.167-13.168), the dimensions of the H-H MO can 15 be solved.

The most convenient way to solve Eq. (13.361) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 4.9500a_0 = 2.6194 \ X \ 10^{-10} \ m \tag{13.362}$$

Substitution of Eq. (13.362) into Eq. (13.359) gives

$$c' = 1.5732a_0 = 8.3251 \times 10^{-11} m \tag{13.363}$$

The internuclear distance given by multiplying Eq. (13.363) by two is

$$2c' = 3.1464a_0 = 1.6650 X 10^{-10} m ag{13.364}$$

Substitution of Eqs. (13.362-13.363) into Eq. (13.167) gives

$$b = c = 4.6933a_0 = 2.4836 X 10^{-10} m ag{13.365}$$

25 Substitution of Eqs. (13.362-13.363) into Eq. (13.168) gives

$$e = 0.3178 \tag{13.366}$$

Using,  $2c'_{H-H}$  (Eq. (13.364)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (13.361)), and  $2c'_{N-H}$  (Eq. (13.325)), the internuclear distance of each N-H bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle  $\theta$  between the N-H bonds is

$$\theta = \cos^{-1}\left(\frac{2(1.9703)^2 - (3.1464)^2}{2(1.9703)^2}\right)$$

$$= \cos^{-1}(-0.2751) = 105.969^{\circ}$$
(13.367)

The experimental angle between the N-H bonds is [32]

$$\theta = 103.3^{\circ}$$
 (13.368)

The results of the determination of bond parameters of  $NH_2$  and  $ND_2$  are given in 10 Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

#### AMMONIA (NH<sub>3</sub>)

15 Ammonia (NH<sub>3</sub>) is formed by the reaction of a hydrogen atom with a dihydrogen nitride radical:

$$NH_2 + H \rightarrow NH_3 \tag{13.369}$$

 $NH_3$  can be solved using the same principles as those used to solve  $NH_2$  except that three rather than two  $H_2$ -type prolate spheroidal molecular orbitals (MOs) serve as basis functions 20 in a linear combination with nitrogen atomic orbitals (AOs) to form the MO of  $NH_3$ .

#### FORCE BALANCE OF NH.

 $NH_3$  comprises three chemical bonds between nitrogen and hydrogen. Each N-H bond comprises two spin-paired electrons with one from an initially unpaired electron of the nitrogen atom and the other from the hydrogen atom. Each H-atom electron forms a  $H_2$ -type ellipsoidal MO with one of the initially unpaired N-atom electrons,  $2p_x$ ,  $2p_y$ , or  $2p_z$ , such that the proton and the N nucleus serve as the foci. The initial N electron configuration given in the Seven-Electron Atoms section is  $1s^2 2s^2 2p^3$ , and the orbital

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arrangement is given by Eqs. (10.134) and (13.246). The radius and the energy of the N2p shell are unchanged with bond formation. The central paramagnetic force due to spin of each N-H bond is provided by the spin-paring force of the  $NH_3$  MO that has the symmetry of an s orbital that superimposes with the N2p orbitals such that the corresponding angular 5 momenta are unchanged.

As in the case of  $H_2$ , each of three N-H-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the N atom for distances shorter than the radius of the 2p shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at each H proton that is continuous with the 2p shell at 10 the N atom. The energies in the  $NH_3$  MO involve only each N2p and each H1s electron with the formation of each N-H bond. The sum of the energies of the prolate spheroids is matched to that of the 2p shell. The forces are determined by these energies. As in the cases of NH and  $NH_2$ , the linear combination of each  $H_2$ -type ellipsoidal MO with each N2p AO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the N2p 15 AO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $NH_3$  MO must comprise three N-H bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO (1/2+25%) and a nitrogen AO:

$$[1 N2p_x AO + 0.75 H_2 MO] + [1 N2p_y AO + 0.75 H_2 MO] + [1 N2p_z AO + 0.75 H_2 MO]$$
  
 $\rightarrow NH, MO$ 

(13.370)

The force constant k' of the each H<sub>2</sub>-type-ellipsoidal-MO component of the NH<sub>3</sub> MO is given by Eq. (13.248). The distance from the origin of each N-H-bond MO to each focus c' is given by Eq. (13.249). The internuclear distance is given by Eq. (13.250). The length of the semiminor axis of the prolate spheroidal N-H-bond MO b = c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each N-H-bond MO. Since each of the three prolate spheroidal N-H-bond MOs comprises a H<sub>2</sub>-type-ellipsoidal MO that transitions to the N AO, the energy E in Eq. (13.251) adds to that of the three corresponding H<sub>2</sub>-type ellipsoidal MOs to give the total energy of the NH<sub>3</sub>

MO. From the energy equation and the relationship between the axes, the dimensions of the  $NH_3$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  are three times those of OH and NH given by Eqs. (13.67-13.73) and 1.5 times those of  $H_2O$  given by Eqs. (13.172-13.178). Similarly to  $H_2O$ , since the each prolate spheroidal  $H_2$ -type MO transitions to the N AO and the energy of the N2p shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.251), the total energy  $E_T(NH_3)$  of the  $NH_3$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the N AO and the three  $H_2$ -type ellipsoidal MOs that forms the  $NH_3$  MO as given by Eq. (13.370):

$$E_{T}(NH_{2}) = E_{T} + E(2p \text{ shell})$$

$$= E_{T} - E(\text{ionization}; N)$$

$$= -3 \frac{e^{2}}{8\pi\epsilon_{0}c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \text{ eV}$$
(13.371)

The three hydrogen atoms and the nitrogen atom can achieve an energy minimum as a linear combination of three  $H_2$ -type ellipsoidal MOs each having the proton and the nitrogen nucleus as the foci. Each N-H-bond MO comprises the same N2p shell of constant energy given by Eq. (13.251). Thus, an energy term of the  $NH_3$  MO is given by the sum of the three  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant nitrogen atom of the linear combination given by Eq. (13.251). The total sum is determined by the energy matching condition of the binding atoms.

In Eq. (13.248), the equipotential condition of the union of each  $H_2$ -type-ellipsoidal20 MO and the N AO was met when the force constant used to determine the ellipsoidal parameter  $e^+$  was normalized by the ratio of the ionization energy of N 14.53414 eV [6] and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). This normalized the force to match that of the Coulombic force alone to meet the force matching condition of the NH MO under the influence of the proton 25 and the N nucleus. The minimum total energy of the  $NH_3$  MO from the sum of energies of a linear combination from four atoms is determined using the energy matching condition of Eq. (13.248). Since each of the three prolate spheroidal N-H-bond MOs of  $NH_3$  comprises a  $H_2$ -type-ellipsoidal MO that transitions to the N AO and the energy matching

condition is met, the nitrogen energy E (Eq. (13.251)) and the energy (Eq. (1.243)) of a hydrogen atomic orbital (H AO),  $E_{Coulomb}(H)$ , corresponding to the Coulombic force of +e from the nitrogen nucleus is subtracted from the sum of the energies of the three corresponding  $H_2$ -type ellipsoidal MOs to given an energy minimum. From another perspective, the electron configuration of  $NH_2$  is equivalent to that of OH and is given by Eq. (10.174).  $NH_2$  serves as a one-electron atom that is energy matched by the H AO as a basis element to minimize the energy of  $NH_3$  in the formation of the third N-H-bond.

$$E_{T}(3H_{2}-N-H) = \begin{cases} -3\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}} \left[ \left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right) \ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2} \right] \\ -E(N2p \ shell) - E_{Coulomb}(H) \end{cases}$$

$$= 3\left(-31.63536831 \ eV\right) - \left(-14.53414 \ eV - 13.605804 \ eV\right)$$

$$= -66.76616 \ eV$$
(13.372)

 $E_T(NH_3)$  given by Eq. (13.371) is set equal to Eq. (13.372), three times the energy of the  $H_2$ -type ellipsoidal MO minus the energy of the N2p shell and the H AO:

$$E_T(NH_3) = -3\frac{e^2}{8\pi\varepsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \ eV = -66.76616 \ eV$$
(13.373)

From the energy relationship given by Eq. (13.373) and the relationship between the axes given by Eqs. (13.248-13.250) and (13.62-13.63), the dimensions of the NH<sub>3</sub> MO can be solved.

Substitution of Eq. (13.249) into Eq. (13.373) gives

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{0.712154aa_0}} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{0.712154aa_0}}{a - \sqrt{0.712154aa_0}} - 1 \right] = e52.23202$$
 (13.374)

The most convenient way to solve Eq. (13.374) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.34750a_0 = 7.13066 X 10^{-11} m ag{13.375}$$

Substitution of Eq. (13.375) into Eq. (13.249) gives

$$c' = 0.97961a_0 = 5.18385 X 10^{-11} m ag{13.376}$$

The internuclear distance given by multiplying Eq. (13.376) by two is

$$2c' = 1.95921a_0 = 1.03677 \ X \ 10^{-10} \ m \tag{13.377}$$

The experimental bond distance is [32]

$$2c' = 1.012 X 10^{-10} m ag{13.378}$$

Substitution of Eqs. (13.375-13.376) into Eq. (13.62) gives

$$b = c = 0.92527a_0 = 4.89633 \ X \ 10^{-11} \ m \tag{13.379}$$

5 Substitution of Eqs. (13.375-13.376) into Eq. (13.63) gives

$$e = 0.72698 \tag{13.380}$$

The nucleus of the H atom and the nucleus of the N atom comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the  $N2p_x$ ,  $N2p_y$ , or  $N2p_z$  AO are given by Eqs. (13.84-13.95), (13.261-13.270), and (13.261-13.270). Using Eqs. (13.375-13.377) and (13.379-13.380), the polar intersection angle  $\theta'$  given by Eq. (13.261) with  $r_n = r_7 = 0.93084a_0$  is

$$\theta' = 115.89^{\circ}$$
 (13.381)

Then, the angle  $\theta_{N2pAO}$  the radial vector of the  $N2p_x$ ,  $N2p_y$ , or  $N2p_z$  AO makes with the internuclear axis is

15 
$$\theta_{N2pAO} = 180^{\circ} - 115.89^{\circ} = 64.11^{\circ}$$
 (13.382)

as shown in Figure 10. The angle  $\theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the N radial vector given by Eqs. (13.264-13.265), (13.379), and (13.382) is

$$\theta_{H_2MO} = 64.83^{\circ}$$
 (13.383)

20 Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.267), (13.375), and (13.383) is

$$d_{H-MO} = 0.57314a_0 = 3.03292 \ X \ 10^{-11} \ m \tag{13.384}$$

The distance  $d_{N2pAO}$  along the internuclear axis from the origin of the N atom to the point of intersection of the orbitals given by Eqs. (13.269), (13.376), and (13.384) is

$$d_{N2pAO} = 0.40647a_0 = 2.15093 \ X \ 10^{-11} \ m \tag{13.385}$$

As shown in Eq. (13.370), in addition to the p-orbital charge-density modulation, the uniform charge-density in the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals is increased by a factor of 0.25 and the H atoms are each decreased by a factor of 0.25. Using the orbital composition of  $NH_3$  (Eq.

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(13.370)), the radii of Nls = 0.14605a<sub>0</sub> (Eq. (10.51)), N2s = 0.69385a<sub>0</sub> (Eq. (10.62)), and N2p = 0.93084a<sub>0</sub> (Eq. (10.142)) shells, and the parameters of the NH<sub>3</sub> MO given by Eqs. (13.3-13.4) and (13.375-13.385), the charge-density of the NH<sub>3</sub> MO comprising the linear combination of three N-H-bond MOs (NH-type ellipsoidal MOs given in the Energies of NH section) according to Eq. (13.370) is shown in Figure 13. Each N-H-bond MO comprises a H<sub>2</sub>-type ellipsoidal MO and an N2p AO having the dimensional diagram shown in Figure 10.

#### ENERGIES OF NH3

10 The energies of  $NH_3$  given by the substitution of the semiprincipal axes ((Eqs. (13.375-13.377) and (13.379)) into the energy equations (Eqs. (13.67-13.73)) multiplied by three are

$$V_e = 3\left(\frac{3}{4}\right) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -115.28799 \ eV \tag{13.386}$$

$$V_p = 3 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 41.66718 \ eV \tag{13.387}$$

$$T = 3\left(\frac{3}{4}\right) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 42.77848 \, eV \tag{13.388}$$

15 
$$V_m = 3\left(\frac{3}{4}\right) \frac{-\hbar^2}{4m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -21.38924 \ eV \tag{13.389}$$

$$E_{T}(NH_{3}) = -3\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \ eV = -66.76571 \ eV$$
(13.390)

where  $E_T(NH_3)$  is given by Eq. (13.371) which is reiteratively matched to Eq. (13.372) within five-significant-figure round-off error.

### VIBRATION OF NH,

20

The vibrational energy levels of  $NH_3$  may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as

given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

### THE DOPPLER ENERGY TERM OF NH,

5 The radiation reaction force in the case of the vibration of  $NH_3$  in the transition state corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) and Eqs. (13.22) and (13.144) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. The equations of the radiation reaction force of ammonia are the same as those of the corresponding water and dihydrogen and dideuterium nitride radicals with the substitution of the ammonia parameters. Using Eqs. (11.136) and (13.207-13.209), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 5.68887 \, X \, 10^{16} \, rad/s \tag{13.391}$$

where b is given by Eq. (13.379). The kinetic energy,  $E_K$ , is given by Planck's equation 15 (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 5.68887 \, X \, 10^{16} \, rad \, / \, s = 37.44514 \, eV$$
 (13.392)

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO acting independently due to the  $D_{3h}$  symmetry point group, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.392) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.6353683 \ eV \sqrt{\frac{2e(37.44514 \ eV)}{m_e c^2}} = -0.38298 \ eV \tag{13.393}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $NH_3$  due to 25 the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{asc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (13.393) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational

energy of  $NH_3$ . Using the experimental  $^{14}NH_3$  vibrational energy of  $E_{vib} = 3443.59 \ cm^{-1} = 0.426954 \ eV$  [36] gives

$$\overline{E}'_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.394)

$$\overline{E}'_{osc} = -0.38298 \ eV + \frac{1}{2} (0.426954 \ eV) = -0.16950 \ eV$$
 (13.395)

5 per bond. The reentrant orbit for the binding of a hydrogen atom to a  $NH_2$  radical involves three N-H bonds. Since the vibration and reentrant oscillation is along three bonds,  $\overline{E}_{osc}$  for  $^{14}NH_3$ ,  $\overline{E}_{osc}(^{14}NH_3)$ , is:

$$\overline{E}_{asc} \left( {}^{14}NH_3 \right) = 3 \left( \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) 
= 3 \left( -0.38298 \ eV + \frac{1}{2} \left( 0.426954 \ eV \right) \right) 
= -0.50850 \ eV$$
(13.396)

Using Eq. (13.393), Eqs. (13.394-13.396), and the  $^{14}ND_3$  experimental vibrational 10 energy of  $E_{vib} = 2563.96 \ cm^{-1} = 0.317893 \ eV$  [36], the corresponding  $\overline{E}_{osc} \left(^{14}ND_2\right)$  is

$$\overline{E}_{osc}(^{14}ND_3) = 3\left(-0.38298 \ eV + \frac{1}{2}(0.317893 \ eV)\right)$$

$$= -0.67209 \ eV$$
(13.397)

# TOTAL AND BOND ENERGIES OF "NH, AND "ND,

 $E_{T+osc}(^{14}NH_3)$ , the total energy of the  $^{14}NH_3$  including the Doppler term, is given by the sum 15 of  $E_T(NH_3)$  (Eq. (13.373)) and  $\overline{E}_{osc}(^{14}NH_3)$  given Eqs. (13.391-13.396):

$$E_{T+osc}(^{14}NH_{3}) = V_{e} + T + V_{m} + V_{p} + E(N2p) + \overline{E}_{osc}(^{14}NH_{3})$$

$$= E_{T}(NH_{3}) + \overline{E}_{osc}(^{14}NH_{3})$$
(13.398)

$$E_{T+osc}(^{14}NH_3) = \begin{cases} 3\frac{-e^2}{8\pi\varepsilon_0 c'} \left[ \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.53414 \, eV \right] \\ -3\left( (31.63536831 \, eV) \sqrt{\frac{2\hbar\sqrt{\frac{3}{2} \frac{e^2}{4\pi\varepsilon_0 b^3}}}{\frac{m_e}{m_e c^2}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}} \right) \end{cases}$$

$$= -66.76616 \, eV - 3\left( 0.38298 \, eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right)$$

$$(13.399)$$

From Eqs. (13.396) and (13.398-13.399), the total energy of  $^{14}NH_2$  is

$$E_{T+osc}(^{14}NH_3) = -66.76616 \ eV + \overline{E}_{osc}(^{14}NH_3)$$

$$= -66.76616 \ eV - 3\left(0.38298 \ eV - \frac{1}{2}(0.426954 \ eV)\right)$$

$$= -67.27466 \ eV$$
(13.400)

where the experimental  $^{14}NH_3$  vibrational energy was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

5  $E_{T+osc}(^{14}ND_3)$ , the total energy of  $^{14}ND_3$  including the Doppler term is given by the sum of  $E_T(ND_3) = E_T(NH_3)$  (Eq. (13.373)) and  $\overline{E}_{osc}(^{14}ND_3)$  given by Eq. (13.397):

$$E_{T+osc}(^{14}ND_3) = -66.76616 \ eV + \overline{E}_{osc}(^{14}ND_3)$$

$$= -66.76616 \ eV - 3\left(0.38298 \ eV - \frac{1}{2}(0.317893 \ eV)\right)$$

$$= -67.43780 \ eV$$
(13.401)

where the experimental  $^{14}ND_3$  vibrational energy was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term. The corresponding bond dissociation energy,  $E_D$ , is given by the sum of the total energies of the 10 corresponding dihydrogen nitride radical and hydrogen atom minus the total energy of ammonia,  $E_{T+ose}(^{14}NH_3)$ .

Thus,  $E_D$  of  $^{14}NH_3$  is given by:

$$E_{D}(^{14}NH_{3}) = E(H) + E(^{14}NH_{2}) - E_{T+osc}(^{14}NH_{3})$$
(13.402)

where  $E_T(^{14}NH_2)$  is given by the of the sum of the experimental energies of  $^{14}N$  (Eq. 15 (13.251)), two H (Eq. (13.154)), and the negative of the bond energies of  $^{14}NH$  (Eq. (13.312)) and  $^{14}NH_2$  (Eq. (13.354)):

$$E(^{14}NH_2) = 2(-13.59844 \ eV) - 14.53414 \ eV - 3.42 \ eV - 3.946 \ eV = -49.09709 \ eV$$
(13.403)

From Eqs. (13.154), (13.400), and (13.402-13.403),  $E_D(^{14}NH_2)$  is

$$E_{D}(^{14}NH_{3}) = E(H) + E(^{14}NH_{2}) - E_{T+osc}(^{14}NH_{3})$$

$$= -13.59844 \ eV - 49.09709 \ eV - (-67.27466 \ eV)$$

$$= 4.57913 \ eV$$
(13.404)

5 The experimental  $^{14}NH_3$  bond dissociation energy [37] is

$$E_D(^{14}NH_3) = 4.60155 \ eV \tag{13.405}$$

Similarly,  $E_D$  of <sup>14</sup>ND<sub>3</sub> is given by:

$$E_D(^{14}ND_3) = E(D) + E(^{14}ND_2) - (E_{T+asc}(^{14}ND_3))$$
(13.406)

where  $E_T(^{14}ND_2)$  is given by the of the sum of the experimental energies of  $^{14}N$  (Eq. 10 (13.251)), two times the energy of D (Eq. (13.155)), and the negative of the bond energies of  $^{14}ND$  (Eq. (13.315)) and  $^{14}ND_2$  (Eq. (13.358)):

$$E(^{14}ND_2) = 2(-13.603 \ eV) - 14.53414 \ eV - 3.5134 \ eV - 3.9362 \ eV = -49.18981 \ eV$$
(13.407)

From Eqs. (13.155), (13.401), and (13.406-13.407),  $E_D(^{14}ND_3)$  is

15 
$$E_D(^{14}ND_3) = -13.603 \ eV - 49.18981 \ eV - (-67.43780 \ eV) = 4.64499 \ eV$$
 (13.408)

The experimental <sup>14</sup>ND<sub>3</sub> bond dissociation energy [37] is

$$E_D(^{14}ND_3) = 4.71252 \ eV \tag{13.409}$$

## BOND ANGLE OF NH3

Using,  $2c'_{H-H}$  (Eq. (13.364)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (13.361)), and  $2c'_{N-H}$ , the internuclear distance of each N-H bond (Eq. (13.377)), the corresponding bond angle can be determined from the law of cosines. Using Eq. (13.367), the bond angle  $\theta$  between the N-H bonds is

$$\theta = \cos^{-1}\left(\frac{2(1.95921)^2 - (3.14643)^2}{2(1.95921)^2}\right) = \cos^{-1}(-0.28956) = 106.67^{\circ}$$
 (13.410)

25 The experimental angle between the N-H bonds is [36]

5 atom is given by

$$\theta = 106.67^{\circ}$$
 (13.411)

The  $NH_3$  molecule has a pyramidal structure with the nitrogen atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. Since any two N-H bonds form an isosceles triangle, the distance  $d_{origin-H}$  from the origin to the nucleus of a hydrogen

$$d_{origin-H} = \frac{2c'_{H-H}}{2\sin 60^{\circ}} \tag{13.412}$$

Substitution of Eq. (13.364) into Eq. (13.412) gives

$$d_{origin-H} = 1.81659a_0 (13.413)$$

The height along the z-axis of the pyramid from the origin to N nucleus  $d_{height}$  is given by

$$d_{height} = \sqrt{(2c'_{N-H})^2 - (d_{origin-H})^2}$$
 (13.414)

Substitution of Eqs. (13.377) and (13.413) into Eq. (13.414) gives

$$d_{height} = 0.73383a_0 \tag{13.415}$$

The angle  $\theta_{r}$  of each N-H bond from the z-axis is given by

$$\theta_{\nu} = \tan^{-1} \left( \frac{d_{origin-H}}{d_{height}} \right) \tag{13.416}$$

15 Substitution of Eqs. (13.413) and (13.415) into Eq. (13.417) gives

$$\theta_{\rm v} = 68.00^{\circ}$$
 (13.417)

The  $NH_3$  MO shown in Figure 13 was rendered using these parameters.

The results of the determination of bond parameters of NH<sub>3</sub> and ND<sub>3</sub> are given in Table 13.1. The calculated results are based on first principles and given in closed-form, 20 exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## HYDROGEN CARBIDE (CH)

The methane molecule can be solved by first considering the solution of the hydrogen 25 carbide, dihydrogen carbide, and methyl radicals. The former is formed by the reaction of a hydrogen atom and a carbon atom:

$$H + C \to CH \tag{13.418}$$

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The hydrogen carbide radicals, CH and  $CH_2$ , methyl radical,  $CH_3$ , and methane,  $CH_4$ , can be solved using the same principles as those used to solve OH,  $H_2O$ , NH,  $NH_2$ , and  $NH_3$  with the exception that the carbon 2s and 2p shells hybridize to form a single  $2sp^3$  shell as an energy minimum.

5

#### FORCE BALANCE OF CH

CH comprises two spin-paired electrons in a chemical bond between the carbon atom and the hydrogen atom. The CH radical molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal  $H_2$  MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the H-atom electron forms a  $H_2$ -type ellipsoidal MO with one of the C-atom electrons. However, such a bond is not possible with the outer C electrons in their ground state since the resulting  $H_2$ -type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon 2p shell, which is not energetically stable. Thus, when bonding the carbon 2s and 2p shells hybridize to form a single  $2sp^3$  shell as an energy minimum.

The C electron configuration given in the Six-Electron Atoms section is  $1s^2 2s^2 2p^2$ , and the orbital arrangement is

$$\begin{array}{c|c}
2p \text{ state} \\
\uparrow & \uparrow \\
\hline
1 & 0 & -1
\end{array}$$
(13.419)

20 corresponding to the ground state  ${}^{3}P_{0}$ . The radius  $r_{6}$  of the 2p shell given by Eq. (10.122) is  $r_{6} = 1.20654a_{0}$  (13.420)

The energy of the carbon 2p shell is the negative of the ionization energy of the carbon atom given by Eq. (10.123). Experimentally, the energy is [12]

$$E(C,2p \text{ shell}) = -E(\text{ionization}; C) = -11.2603 \text{ eV}$$
(13.421)

25 The C2s atomic orbital (AO) combines with the C2p AOs to form a single  $2sp^3$  hybridized orbital (HO) with the orbital arrangement

where the quantum numbers  $(\ell, m_\ell)$  are below each electron. The total energy of the state is given by the sum over the four electrons. The sum  $E_T(C,2sp^3)$  of calculated energies of C, 5  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is  $E_T(C,2sp^3)=64.3921~eV+48.3125~eV+24.2762~eV+11.27671~eV=148.25751~eV$  (13.423)

which agrees well with the sum of  $148.02532 \, eV$  from the experimental [6] values. The orbital-angular-momentum interactions cancel such that the energy of the  $E_T(C, 2sp^3)$  is 10 purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{2sp^3}$  of the  $C2sp^3$  shell may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{2:p^3} = \sum_{n=2}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0 \left(e148.25751 \, eV\right)} = \frac{10e^2}{8\pi\varepsilon_0 \left(e148.25751 \, eV\right)} = 0.91771a_0 \tag{13.424}$$

Using Eqs. (10.102) and (13.424), the Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  of the outer 15 electron of the  $C2sp^3$  shell is

$$E_{Coulomb}\left(C, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.91771a_{0}} = -14.82575 \ eV \tag{13.425}$$

During hybridization, one of the spin-paired 2s electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152) at the initial radius of the 2s electrons. From Eq. (10.62) with Z=6, the radius  $r_3$  20 of C2s shell is

$$r_3 = 0.84317a_0 \tag{13.426}$$

Using Eqs. (13.152) and (13.426), the unpairing energy is

$$E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.84317a_0)^3} = 0.19086 \ eV$$
 (13.427)

Using Eqs. (13.425) and (13.427), the energy  $E(C, 2sp^3)$  of the outer electron of the  $C2sp^3$ 

shell is

$$E(C,2sp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(r_{3})^{3}}$$

$$= -14.82575 \ eV + 0.19086 \ eV$$

$$= -14.63489 \ eV$$
(13.428)

The nitrogen atom's 2p-shell electron configuration given by Eq. (10.134) is the same as that of the  $C2sp^3$  shell, and nitrogen's calculated energy of 14.61664 eV given by Eq. (10.143) is a close match with  $E(C,2sp^3)$ . Thus, the binding should be very similar except that four bonds to hydrogen can occur with carbon.

The carbon  $C2sp^3$  electron combines with the H1s electron to form a molecular orbital. The proton of the H atom and the nucleus of the C atom are along the internuclear axis and serve as the foci. Due to symmetry, the other C electrons are equivalent to point 10 charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the CH MO involve only the  $C2sp^3$  and H1s electrons. The forces are determined by these energies.

As in the case of  $H_2$ , the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell. Thus, the MO surface comprises a prolate spheroid at the H proton that is continuous with the  $C2sp^3$  shell at the C atom whose nucleus serves as the other focus. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  shell. As in the case with OH and NH, the linear combination of the  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  HO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $C2sp^3$  HO in order to match potential, kinetic, and orbital energy relationships. Thus, the CH MO must comprise 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO:

$$1 C2sp^3 + 0.75 H_2 MO \rightarrow CH MO$$
 (13.429)

The force balance of the CH MO is determined by the boundary conditions that arise from 25 the linear combination of orbitals according to Eq. (13.429) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

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As in the case with OH (Eq. (13.57)), the  $H_2$ -type ellipsoidal MO comprises 75% of the CH MO; so, the electron charge density in Eq. (11.65) is given by -0.75e. The force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the CH MO. Since the CH MO comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $C2sp^3$  HO, the energy  $E(C,2sp^3)$  in Eq. (13.428) adds to that of the  $E(C,2sp^3)$  in Eq. (13.428) adds to that of the  $E(C,2sp^3)$  between the axes, the dimensions of the  $E(C,2sp^3)$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ , T, and  $V_m$  are those of  $H_2$  (Eqs. (11.207-11.212)) except that they are corrected for electron hybridization. Hybridization gives rise to the 15  $C2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}\left(C,2sp^3\right)$  given by Eq. (13.425). To meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the  $C2sp^3$  HO, the electron energies are normalized by the ratio of 14.82575 eV, the magnitude of  $E_{Coulomb}\left(C,2sp^3\right)$  given by Eq. (13.425), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). This normalizes the 20 energies to match that of the Coulombic energy alone to meet the energy matching condition of the CH MO under the influence of the proton and the C nucleus. The hybridization energy factor  $C_{C2sp^3HO}$  is

$$C_{C2sp^3HO} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{2sp^3}}} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.91771a_0}} = \frac{13.605804 \ eV}{14.82575 \ eV} = 0.91771$$
 (13.430)

The total energy  $E_T(CH)$  of the CH MO is given by the sum of the energies of the orbitals, 25 the  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO, that form the hybridized CH MO.  $E_T(CH)$  follows from by Eq. (13.74) for OH, but the energy of the  $C2sp^3$  HO given by Eq. (13.428) is substituted for the energy of O and the  $H_2$ -type-ellipsoidal-MO energies are

those of  $H_2$  (Eqs. (11.207-11.212)) multiplied by the electron hybridization factor rather than by the factor of 0.75:

$$E_{T}(CH) = E_{T} + E(C, 2sp^{3}) = -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \ eV$$
(13.431)

To match the boundary condition that the total energy of the entire the  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75),  $E_T(CH)$  given by Eq. (13.431) is set equal to Eq. (13.75):

$$E_T(CH) = -\frac{e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \ eV = -31.63536831 \ eV$$

From the energy relationship given by Eq. (13.432) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.432) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e17.00048$$
(13.433)

15 The most convenient way to solve Eq. (13.433) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.67465a_0 = 8.86186 X 10^{-11} m ag{13.434}$$

Substitution of Eq. (13.434) into Eq. (13.60) gives

$$c' = 1.05661a_0 = 5.59136 \times 10^{-11} m \tag{13.435}$$

20 The internuclear distance given by multiplying Eq. (13.435) by two is

$$2c' = 2.11323a_0 = 1.11827 \ X \ 10^{-10} \ m \tag{13.436}$$

The experimental bond distance is [14]

5

10

$$2c' = 1.1198 X 10^{-10} m ag{13.437}$$

Substitution of Eqs. (13.434-13.435) into Eq. (13.62) gives

25 
$$b = c = 1.29924a_0 = 6.87527 \times 10^{-11} m$$
 (13.438)

Substitution of Eqs. (13.434-13.435) into Eq. (13.63) gives

$$e = 0.63095 \tag{13.439}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta^1$  is given by Eq. (13.261) where  $r_n = r_{2sp^3} = 0.91771a_0$  is the radius of the

5 C2sp<sup>3</sup> shell. Substitution of Eqs. (13.434-13.435) into Eq. (13.261) gives

$$\theta' = 81.03^{\circ}$$
 (13.440)

Then, the angle  $\theta_{C2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C2m^3HO} = 180^{\circ} - 81.03^{\circ} = 98.97^{\circ} \tag{13.441}$$

10 as shown in Figure 14.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  radial vector obeys the following relationship:

$$r_{2sp^3} \sin \theta_{C2sp^3HO} = 0.91771a_0 \sin \theta_{C2sp^3HO} = b \sin \theta_{H_2MO}$$
 (13.442)

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{0.91771 a_0 \sin \theta_{C2sp^3HO}}{b} = \sin^{-1} \frac{0.91771 a_0 \sin 98.97^{\circ}}{b}$$
(13.443)

with the use of Eq. (13.441). Substitution of Eq. (13.438) into Eq. (13.443) gives

$$\theta_{H_2MO} = 44.24^{\circ} \tag{13.444}$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.445}$$

Substitution of Eqs. (13.434) and (13.444) into Eq. (13.445) gives

$$d_{H,MO} = 1.19968a_0 = 6.34845 X 10^{-11} m ag{13.446}$$

The distance  $d_{C2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C2xp^3HO} = d_{H,MO} - c' (13.447)$$

Substitution of Eqs. (13.435) and (13.446) into Eq. (13.447) gives

$$d_{C2m^3H0} = 0.14307a_0 = 7.57090 X 10^{-12} m ag{13.448}$$

As shown in Eq. (13.429), the uniform charge-density in the  $C2sp^3$  HO is increased by a factor of 0.25 and the H-atom density is decreased by a factor of 0.25. Using the orbital composition of CH (Eq. (13.429)), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and

5  $C2sp^3 = 0.91771a_0$  (Eq. (10.424)) shells, and the parameters of the CH MO given by Eqs. (13.3-13.4), (13.434-13.436), and (13.438-13.448), the dimensional diagram and chargedensity of the CH MO comprising the linear combination of the  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO according to Eq. (13.429) are shown in Figures 14 and 15, respectively.

10

#### ENERGIES OF CH

The energies of CH are given by the substitution of the semiprincipal axes (Eqs. (13.434-13.435) and (13.438)) into the energy equations, (Eq. (13.431) and Eqs. (11.207-11.211) that are corrected for electron hybridization using Eq. (13.430):

15 
$$V_e = (0.91771) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -35.12015 \ eV \tag{13.449}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 12.87680 \ eV \tag{13.450}$$

$$T = (0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 10.48582 \ eV$$
 (13.451)

$$V_{m} = (0.91771) \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} = -5.24291 \ eV$$
 (13.452)

$$E_T(CH) = -\frac{e^2}{8\pi\varepsilon_0 c'} \left[ \left( 0.91771 \right) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \ eV = -31.63533 \ eV$$

20 (13.453)

where  $E_T(CH)$  is given by Eq. (13.431) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

## VIBRATION AND ROTATION OF CH

The vibrational energy of CH may be solved in the same manner as that of OH and NH except that the force between the electrons and the foci given by Eq. (13.102) is doubled due to electron hybridization of the two shells of carbon after Eq. (11.141). From Eqs. (13.102-13.106) with the substitution of the CH parameters, the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3} - \frac{e^2}{8\pi\varepsilon_0 (2c')^3}}{\mu}}$$

$$= \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 (1.29924a_0)^3} - \frac{e^2}{8\pi\varepsilon_0 (2.11323a_0)^3}}{\frac{12}{13}m_p}}$$

$$= 5.39828 \times 10^{14} \ rad/s$$
(13.454)

where b is given by Eq. (13.438), 2c' is given by Eq. (13.436), and the reduced mass of  $^{12}CH$  is given by:

10 
$$\mu_{12_{CH}} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1)(12)}{1 + 12} m_p \tag{13.455}$$

where  $m_p$  is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency,  $\omega(0)$ , for <sup>12</sup>CH given by Eqs. (11.136), (11.148), and (13.454) is

15 
$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{449.94 \ Nm^{-1}}{\mu}} = 5.39828 \ X \ 10^{14} \ radians / s$$
 (13.456)

where the reduced nuclear mass of  $^{12}CH$  is given by Eq.(13.455) and the spring constant, k(0), given by Eqs. (11.136) and (13.454) is

$$k(0) = 449.94 \, Nm^{-1} \tag{13.457}$$

The  $^{12}CH$  transition-state vibrational energy,  $E_{vib}(0)$ , given by Planck's equation (Eq. 20 (11.127)) is:

$$E_{vib}(0) = \hbar\omega = \hbar 5.39828 \ X \ 10^{14} \ rad/s = 0.35532 \ eV = 2865.86 \ cm^{-1}$$
 (13.458)

 $\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{12}CH$  is [14]

$$\omega_e = 2861.6 \ cm^{-1} \tag{13.459}$$

Using Eqs. (13.112-13.118) with  $E_{vib}(0)$  given by Eq. (13.458) and  $D_0$  given by Eq. (13.488), the  $^{12}CH$   $\upsilon=1\rightarrow\upsilon=0$  vibrational energy,  $E_{vib}(1)$  is

$$E_{vib}(1) = 0.33879 \ eV$$
 (2732.61 cm<sup>-1</sup>) (13.460)

5 The experimental vibrational energy of  $^{12}CH$  using  $\omega_e$  and  $\omega_e x_e$  [14] according to K&P [15] is

$$E_{vib}(1) = 0.33885 \ eV$$
 (2733 cm<sup>-1</sup>) (13.461)

Using Eq. (13.113) with  $E_{vib}$  (1) given by Eq. (13.460) and  $D_0$  given by Eq. (13.488), the anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{12}CH$  is

$$\omega_0 x_0 = 66.624 \ cm^{-1} \tag{13.462}$$

The experimental anharmonic perturbation term,  $\omega_0 x_0$ , of <sup>12</sup>CH [14] is

$$\omega_0 x_0 = 64.3 \ cm^{-1} \tag{13.463}$$

The vibrational energies of successive states are given by Eqs. (13.458), (13.112), and (13.462).

15 Using b given by Eq. (13.438), 2c' given by Eq. (13.436),  $D_0$  given by Eq. (13.490), and the reduced nuclear mass of  $^{12}CD$  given by

$$\mu_{u_{CD}} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(12)}{2 + 12} m_p \tag{13.464}$$

where  $m_p$  is the proton mass, the corresponding parameters for deuterium carbide  $^{12}CD$  (Eqs. (13.102-13.121)) are

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{449.94 \ Nm^{-1}}{\mu}} = 3.96126 \ X \ 10^{14} \ radians / s \tag{13.465}$$

$$k(0) = 449.94 \ Nm^{-1} \tag{13.466}$$

$$E_{vib}(0) = \hbar\omega = \hbar 3.96126 X 10^{14} \ rad/s = 0.26074 \ eV = 2102.97 \ cm^{-1}$$
 (13.467)

$$E_{vib}(1) = 0.25173 \ eV$$
 (2030.30 cm<sup>-1</sup>) (13.468)

$$\omega_0 x_0 = 36.335 \ cm^{-1} \tag{13.469}$$

25  $\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{12}CD$  is [14]

$$\omega_e = 2101.0 \ cm^{-1} \tag{13.470}$$

The experimental vibrational energy of  $^{12}CD$  using  $\omega_e$  and  $\omega_e x_e$  [14] according to K&P [15] is

$$E_{vib}(1) = 0.25189 \ eV$$
 (2031.6 cm<sup>-1</sup>) (13.471)

and the experimental anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{12}CD$  is [14]

$$\delta \omega_0 x_0 = 34.7 \ cm^{-1} \tag{13.472}$$

which match the predictions given by Eqs. (13.467), (13.468) and (13.469), respectively.

Using Eqs. (13.133-13.134) and the internuclear distance, r = 2c', and reduced mass of  $^{12}CH$  given by Eqs. (13.436) and (13.455), respectively, the corresponding  $B_e$  is

$$B_e = 14.498 \ cm^{-1} \tag{13.473}$$

10 The experimental  $B_e$  rotational parameter of  $^{12}CH$  is [14]

$$B_e = 14.457 \text{ cm}^{-1} \tag{13.474}$$

Using the internuclear distance,  $r = 2c^{-1}$ , and reduced mass of  $^{12}CD$  given by Eqs. (13.436) and (13.464), respectively, the corresponding  $B_e$  is

$$B_e = 7.807 \ cm^{-1} \tag{13.475}$$

15 The experimental  $B_e$  rotational parameter of  $^{12}CD$  is [14]

$$B_e = 7.808 \ cm^{-1} \tag{13.476}$$

### THE DOPPLER ENERGY TERMS OF 12CH AND 12CD

The equations of the radiation reaction force of hydrogen and deuterium carbide are the same 20 as those of the corresponding hydroxyl and hydrogen nitride radicals with the substitution of the hydrogen and deuterium carbide parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}} = 2.41759 \, X \, 10^{16} \, rad/s \tag{13.477}$$

where b is given by Eq. (13.438). The kinetic energy,  $E_{\kappa}$ , is given by Planck's equation 25 (Eq. (11.127)):

$$\overline{E}_K = \hbar \omega = \hbar 2.41759 \, X \, 10^{16} \, rad \, / \, s = 15.91299 \, eV$$
 (13.478)

In Eq. (11.181), substitution of the total energy of CH,  $E_T(CH)$ , (Eq. (13.432)) for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.478) for  $\overline{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(15.91299 \ eV)}{m_e c^2}} = -0.24966 \ eV \tag{13.479}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (13.479) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of CH. The experimental  $^{12}CH$   $\omega_e$  is 2861.6  $cm^{-1}$  (0.35480 eV) [14] which matches the predicted  $\omega_e$  of 2865.86  $cm^{-1}$  (0.35532 eV) given by Eq. (13.458). Using the predicted  $\omega_e$  for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{osc}$  ( $^{12}CH$ ) is

$$\overline{E}_{osc}\left(^{12}CH\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.480)

$$\overline{E}_{osc}(^{12}CH) = -0.24966 \ eV + \frac{1}{2}(0.35532 \ eV) = -0.07200 \ eV$$
 (13.481)

15 The experimental  $^{12}CD$   $\omega_e$  is 2101.0 cm $^{-1}$  (0.26049 eV) [14] which matches the predicted  $\omega_e$  of 2102.97 cm $^{-1}$  (0.26074 eV) given by Eq. (13.467). Using Eq. (13.479) and the predicted  $\omega_e$  for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{osc}$  ( $^{12}CD$ ) is

$$\overline{E}_{asc}(^{12}CD) = -0.24966 \ eV + \frac{1}{2}(0.26074 \ eV) = -0.11929 \ eV$$
 (13.482)

20 TOTAL AND BOND ENERGIES OF  $^{12}CH$  AND  $^{12}CD$   $E_{T+osc}(^{12}CH)$ , the total energy of the  $^{12}CH$  radical including the Doppler term, is given by

the sum of  $E_T(CH)$  (Eq. (13.432)) and  $\overline{E}_{osc}(^{12}CH)$  given by Eq. (13.481):

$$E_{T+cose}\left({}^{12}CH\right) = V_e + T + V_m + V_p + E\left(C, 2sp^3\right) + \widetilde{E}_{cose}\left({}^{12}CH\right)$$

$$= E_T\left(CH\right) + \overline{E}_{cose}\left({}^{12}CH\right)$$
(13.483)

$$E_{T+osc}(^{12}CH) = \begin{cases} \left(\frac{-e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left(2 - \frac{1}{2} \frac{a_0}{a}\right) \ln \frac{a+c'}{a-c'} - 1\right] - 14.63489 \ eV \right) \\ \left(\frac{2\hbar\sqrt{\frac{3}{4} \frac{e^2}{4\pi\varepsilon_0 b^3}}}{\frac{m_e}{m_e c^2}} \right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{cases}$$

$$= -31.63537 \ eV - 0.24966 \ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

(13.484)

From Eqs. (13.480-13.481) and (13.483-13.484), the total energy of  $^{12}CH$  is

$$E_{T+osc}(^{12}CH) = -31.63537 \ eV + \overline{E}_{osc}(^{12}CH)$$

$$= -31.63537 \ eV - 0.24966 \ eV + \frac{1}{2}(0.35532 \ eV)$$

$$= -31.70737 \ eV$$
(13.485)

5 where the predicted  $\omega_{\epsilon}$  (Eq. (13.458)) was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.  $E_{T+osc}(^{12}CD)$ , the total energy of  $^{12}CD$  including the Doppler term, is given by the sum of  $E_{T}(CD) = E_{T}(CH)$  (Eq. (13.432)) and  $\overline{E}_{osc}(^{12}CD)$  given by Eq. (13.482):

$$E_{T+ose} \left( {}^{12}CD \right) = -31.63537 \ eV + \overline{E}_{ose} \left( {}^{12}CD \right)$$

$$= -31.63537 \ eV - 0.24966 \ eV + \frac{1}{2} \left( 0.26074 \ eV \right)$$

$$= -31.75462 \ eV$$
(13.486)

where the predicted  $\omega_e$  (Eq. (13.467)) was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

The CH bond dissociation energy,  $E_D(^{12}CH)$ , is given by the sum of the total energies of the  $C2sp^3$  HO and the hydrogen atom minus  $E_{T+osc}(^{12}CH)^3$ :

$$E_D(^{12}CH) = E(C, 2sp^3) + E(H) - E_{T+osc}(^{12}CH)$$
 (13.487)

The hybridization energy is the difference between and  $E(C,2sp^3)$  given by Eq. (13.428) and  $E(C,2p \ shell)$  given by Eq. (13.421). Since this term adds to  $E(C,2p \ shell)$  to give the total energy from which  $E_{r+os}$  ( $^{12}CH$ ) is subtracted to give  $E_p(^{12}CH)$ , it is more convenient to simply use  $E(C,2sp^3)$  directly in Eq. (13.487).

 $E(C,2sp^3)$  is given by Eq. (13.428), and  $E_D(H)$  is given by Eq. (13.154). Thus, the <sup>12</sup>CH bond dissociation energy,  $E_D(^{12}CH)$ , given by Eqs. (13.154), (13.428), (13.485), and (13.487) is

$$E_{D}(^{12}CH) = -(14.63489 \ eV + 13.59844 \ eV) - E_{T+osc}(CH)$$

$$= -28.23333 \ eV - (-31.70737 \ eV)$$

$$= 3.47404 \ eV$$
(13.488)

5 The experimental <sup>12</sup>CH bond dissociation energy is [14]

$$E_D(^{12}CH) = 3.47 \ eV \tag{13.489}$$

which is a close match to that of NH as predicted based on the match between the N and  $C2sp^3$  HO energies and electron configurations.

The  $^{12}CD$  bond dissociation energy,  $E_D(^{12}CD)$ , is given by the sum of the total 10 energies of the  $C2sp^3$  HO and the deuterium atom minus  $E_{T+osc}(CD)$ :

$$E_D(^{12}CD) = E(C, 2sp^3) + E(D) - E_{T+osc}(^{12}CD)$$
 (13.490)

 $E(C, 2sp^3)$  is given by Eq. (13.428), and  $E_D(D)$  is given by Eq. (13.155). Thus, the  $^{12}CD$  bond dissociation energy,  $E_D(^{12}CD)$ , given by Eqs. (13.155), (13.428), (13.486), and (13.490) is

$$E_{D}(^{12}CD) = -(14.63489 \ eV + 13.603 \ eV) - E_{T+osc}(^{12}CD)$$

$$= -28.23789 \ eV - (-31.75462 \ eV)$$

$$= 3.51673 \ eV$$
(13.491)

The experimental <sup>12</sup>CD bond dissociation energy is [14]

$$E_D(^{12}CD) = 3.52 \ eV \tag{13.492}$$

The results of the determination of bond parameters of *CH* and *CD* are given in Table 13.1. The calculated results are based on first principles and given in closed-form, 20 exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## DIHYDROGEN CARBIDE (CH<sub>2</sub>)

15

The dihydrogen carbide radical  $CH_2$  is formed by the reaction of a hydrogen atom with a 25 hydrogen carbide radical:

$$CH + H \rightarrow CH_2 \tag{13.493}$$

 $CH_2$  can be solved using the same principles as those used to solve  $H_2O$  and  $NH_2$  with the exception that the carbon 2s and 2p shells hybridize to form a single  $2sp^3$  shell as an energy minimum. Two diatomic molecular orbitals (MOs) developed in the Nature of the 5 Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with two carbon  $2sp^3$  hybridized orbitals (HOs) to form the MO of  $CH_2$ . The solution is very similar to that of CH except that there are two CH bonds in  $CH_2$ .

#### 10 FORCE BALANCE OF CH,

 $CH_2$  comprises two chemical bonds between carbon and hydrogen atoms. Each C-H bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each H-atom electron forms a  $H_2$ -type ellipsoidal MO with an unpaired C-atom electrons. However, such a bond is not possible with the outer two C electrons in their ground state since the resulting  $H_2$ -type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon 2p shell, which is not energetically stable. Thus, when bonding the carbon 2s and 2p shells hybridize to form a single  $2sp^3$  shell as an energy minimum. The electron configuration and the energy,  $E(C,2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422), and (13.428), respectively.

For each C-H bond, a  $C2sp^3$  electron combines with the H1s electron to form a molecular orbital. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , each of the two C-H-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the  $C2sp^3$  shell at the C atom whose nucleus serves as the other focus. The radius and the energy of the  $C2sp^3$  shell are unchanged with bond formation. The central paramagnetic force due to spin of each C-H bond is provided by

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the spin-pairing force of the  $CH_2$  MO that has the symmetry of an s orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged.

The energies in the  $CH_2$  MO involve only each  $C2sp^3$  and each H1s electron with 5 the formation of each C-H bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. As in the cases with of OH,  $H_2O$ , NH,  $NH_2$ ,  $NH_3$ , and CH the linear combination of each  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  HO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $C2sp^3$  HO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $CH_2$  MO must comprise 10 two C-H bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO:

$$[1 C2sp^3 + 0.75 H_2 MO] + [1 C2sp^3 + 0.75 H_2 MO] \rightarrow CH_2 MO$$
 (13.494)

The force balance of the  $CH_2$  MO is determined by the boundary conditions that arise from 15 the linear combination of orbitals according to Eq. (13.494) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH_2$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each C-H-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each C-H-bond MO. Since each of the two prolate spheroidal C-H-bond MOs comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $C2sp^3$  HO, the energy  $E(C,2sp^3)$  in Eq. (13.428) adds to that of the two corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_2$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_2$  MO are solved.

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The energy components of  $V_e$ ,  $V_p$ , T, and  $V_m$  are twice those of CH corresponding to the two C-H bonds. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C2sp^3$  HO and the energy of the  $C2sp^3$  shell must remain constant and equal to the  $E\left(C,2sp^3\right)$  given by Eq. (13.428), the total energy  $E_T\left(CH_2\right)$  of the  $CH_2$  MO is given by 5 the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C2sp^3$  HO and the two  $H_2$ -type ellipsoidal MOs that forms the  $CH_2$  MO as given by Eq. (13.494). Using Eq. (13.431),  $E_T\left(CH_2\right)$  is given by

$$E_{T}(CH_{2}) = E_{T} + E(C, 2sp^{3})$$

$$= -\frac{e^{2}}{4\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \, eV$$
(13.495)

The two hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as 10 a linear combination of two  $H_2$ -type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the C2sp3 HO-shell Coulombic energy  $E_{Coulomb}(C,2sp^3)$  given by Eq. (13.425). To meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the  $C2sp^3$  HO, the electron energies in Eq. (13.495) were normalized by the ratio of 14.82575 eV, the magnitude of  $E_{Coulomb}(C, 2sp^3)$  given by Eq. 15 (13.425), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each C-H-bond MO under the influence of the proton and the C nucleus. Each C-Hbond MO comprises the same C2sp3 shell having its energy normalized to that of the 20 Coulombic energy between the electron and a charge of +e at the carbon focus of the CH<sub>2</sub> MO. Thus, the energy of the  $CH_2$  MO is also given by the sum of that of the two  $H_2$ -type ellipsoidal given Eq. (11.212) minus the Coulombic  $E_{Coulomb}(H) = -13.605804 \ eV$ , of the redundant +e of the linear combination:

$$E_{T}(2H_{2}-H) = -\frac{e^{2}}{4\pi\varepsilon_{0}a_{0}} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] - E_{Coulomb}(H)$$

$$= 2\left( -31.63536831 \, eV \right) - \left( -13.605804 \, eV \right)$$

$$= -49.66493 \, eV$$
(13.496)

 $E_T(CH_2)$  given by Eq. (13.495) is set equal to two times the energy of the  $H_2$ -type ellipsoidal MO minus the Coulombic energy of H given by Eq. (13.496):

$$E_{T}(CH_{2}) = -\frac{e^{2}}{4\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \ eV = -49.66493 \ eV$$
(13.497)

5 From the energy relationship given by Eq. (13.497) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_2$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.497) gives

$$\frac{e^2}{4\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e35.03004$$
(13.498)

The most convenient way to solve Eq. (13.498) is by the reiterative technique using a 10 computer. The result to within the round-off error with five-significant figures is

$$a = 1.64010a_0 = 8.67903 \ X \ 10^{-11} \ m \tag{13.499}$$

Substitution of Eq. (13.499) into Eq. (13.60) gives

$$c' = 1.04566a_0 = 5.53338 X 10^{-11} m ag{13.500}$$

The internuclear distance given by multiplying Eq. (13.500) by two is

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$$2c' = 2.09132a_0 = 1.10668 \times 10^{-10} m$$
 (13.501)

The experimental bond distance is [38]

$$2c' = 1.111 \ X \ 10^{-10} \ m \tag{13.502}$$

Substitution of Eqs. (13.499-13.500) into Eq. (13.62) gives

$$b = c = 1.26354a_0 = 6.68635 X 10^{-11} m ag{13.503}$$

20 Substitution of Eqs. (13.499-13.500) into Eq. (13.63) gives

$$e = 0.63756 \tag{13.504}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO are given by Eqs. (13.84-13.95), (13.261-13.270), and (13.440-13.448). The polar intersection angle  $\theta^1$  is given by Eq. (13.261) where  $r_n = r_{2sp^3} = 0.91771a_0$  is the radius of the  $C2sp^3$  shell. Substitution of Eqs. (13.499-13.500) into Eq. (13.261) gives

$$\theta' = 84.54^{\circ}$$
 (13.505)

Then, the angle  $\theta_{C2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C2sp^3HO} = 180^{\circ} - 84.54^{\circ} = 95.46^{\circ} \tag{13.506}$$

5 as shown in Figure 14. The angle  $\theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  radial vector given by Eqs. (13.442-13.443), (13.503), and (13.506) is

$$\theta_{H_2MO} = 46.30^{\circ} \tag{13.507}$$

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.499), and (13.507) is

$$d_{H,MO} = 1.13305 a_0 = 5.99585 \ X \ 10^{-11} \ m \tag{13.508}$$

The distance  $d_{C2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.500), and (13.508) is

$$d_{C2sp^3HO} = 0.08739a_0 = 4.62472 \ X \ 10^{-12} \ m \tag{13.509}$$

As shown in Eq. (13.494), the uniform charge-density in the  $C2sp^3$  HO is increased by a factor of 0.25 and the H-atom density is decreased by a factor of 0.25 for by each C-H bond. Using the orbital composition of  $CH_2$  (Eq. (13.494)), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C2sp^3 = 0.91771a_0$  (Eq. (10.424)) shells, and the 20 parameters of the  $CH_2$  MO given by Eqs. (13.3-13.4), (13.499-13.501), and (13.503-13.509), the charge-density of the  $CH_2$  MO comprising the linear combination of two C-H-bond MOs is shown in Figure 16. Each C-H-bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO having the dimensional diagram shown in Figure 14.

## 25 ENERGIES OF CH<sub>2</sub>

The energies of  $CH_2$  are two times those of CH and are given by the substitution of the semiprincipal axes (Eqs. (13.499-13.500) and (13.503)) into the energy equations Eq. (13.495) and (Eqs. (13.449-13.452)) that are multiplied by two:

$$V_{e} = (0.91771) \frac{-2e^{2}}{4\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} \ln \frac{\frac{196}{a + \sqrt{a^{2} - b^{2}}}}{a - \sqrt{a^{2} - b^{2}}} = -72.03287 \, eV$$
 (13.510)

$$V_p = \frac{e^2}{4\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 26.02344 \ eV \tag{13.511}$$

$$T = (0.91771) \frac{\hbar^2}{m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 21.95990 \ eV$$
 (13.512)

$$V_m = (0.91771) \frac{-\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -10.97995 \ eV$$
 (13.513)

$$5 \quad E_T(CH_2) = -\frac{e^2}{4\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \ eV = -49.66437 \ eV$$
(13.514)

where  $E_r(CH_2)$  is given by Eq. (13.495) which is reiteratively matched to Eq. (13.496) within five-significant-figure round-off error.

### 10 VIBRATION OF CH,

The vibrational energy levels of  $CH_2$  may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF 12CH,

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of dihydrogen and dideuterium 20 carbide are the same as those of the corresponding hydrogen carbide radicals with the substitution of the dihydrogen and dideuterium carbide parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}} = 2.52077 \, X \, 10^{16} \, rad/s \tag{13.515}$$

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where b is given by Eq. (13.503). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar \omega = \hbar 2.52077 \, X \, 10^{16} \, rad/s = 16.59214 \, eV$$
 (13.516)

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total 5 energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.516) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(16.59214 \ eV)}{m_e c^2}} = -0.25493 \ eV \tag{13.517}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH_2$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (13.517) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which 15 is 1/2 of the vibrational energy of each C-H bond. Using  $\omega_e$  given by Eq. (13.458) for  $\overline{E}_{Kvib}$  of the transition state having two independent bonds,  $\overline{E}_{osc}^{\dagger}$  (12 $CH_2$ ) per bond is

$$\overline{E}'_{osc}\left(^{12}CH_{2}\right) = \overline{E}_{D} + \overline{E}_{Kvib} = \overline{E}_{D} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.518)

$$\overline{E}'_{osc}(^{12}CH_2) = -0.25493 \ eV + \frac{1}{2}(0.35532 \ eV) = -0.07727 \ eV$$
 (13.519)

Given that the vibration and reentrant oscillation is for two C-H bonds,  $\overline{E}_{asc}(^{12}CH_2)$ , is:

$$\overline{E}_{osc} \left( {}^{12}CH_2 \right) = 2 \left( \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) 
= 2 \left( -0.25493 \ eV + \frac{1}{2} \left( 0.35532 \ eV \right) \right) 
= -0.15454 \ eV$$
(13.520)

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## TOTAL AND BOND ENERGIES OF 12CH2

 $E_{T+oso}(^{12}CH_2)$ , the total energy of the  $^{12}CH_2$  radical including the Doppler term, is given by the sum of  $E_T(CH_2)$  (Eq. (13.497)) and  $\overline{E}_{osc}(^{12}CH_2)$  given by Eq. (13.520):

$$E_{T+osc}(CH_2) = V_e + T + V_m + V_p + E(C, 2sp^3) + \overline{E}_{osc}(^{12}CH_2)$$

$$= E_T(CH_2) + \overline{E}_{osc}(^{12}CH_2)$$
(13.521)

$$E_{T+osc}(^{12}CH_{2}) = \begin{cases} \left(\frac{-e^{2}}{4\pi\varepsilon_{0}c'} \left[ (0.91771) \left(2 - \frac{1}{2} \frac{a_{0}}{a}\right) \ln \frac{a+c'}{a-c'} - 1\right] - 14.63489 \ eV\right) \\ \left(-2 \left(31.63536831 \ eV\right) \sqrt{\frac{2\hbar\sqrt{\frac{3}{4} \frac{e^{2}}{44\pi\varepsilon_{0}b^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}} \right) \end{cases}$$

$$= -49.66493 \ eV - 2 \left(0.25493 \ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$(13.522)$$

From Eqs. (13.518-13.522), the total energy of  $^{12}CH_2$  is

$$E_{T+osc}(^{12}CH_2) = -49.66493 \ eV + \overline{E}_{osc}(^{12}CH_2)$$

$$= -49.66493 \ eV - 2\left(0.25493 \ eV - \frac{1}{2}(0.35532 \ eV)\right)$$

$$= -49.81948 \ eV$$
(13.523)

where  $\omega_{\epsilon}$  given by Eq. (13.458) was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

<sup>12</sup>CH<sub>2</sub> has the same electronic configuration as <sup>14</sup>NH. The dissociation of the bond of the dihydrogen carbide radical forms a free hydrogen atom with one unpaired electron and a C2sp<sup>3</sup> HO with three unpaired electrons as shown in Eq. (13.422) wherein the magnetic moments cannot all cancel. Thus, the bond dissociation of <sup>12</sup>CH<sub>2</sub> gives rise to <sup>12</sup>CH with the same electronic configuration as N as given by Eq. (10.134). The N configuration is more stable than H as shown in Eqs. (10.141-10.143). The lowering of the energy of the reactants decreases the bond energy. The total energy of carbon is reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.424):

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 \left(r_{2sp^3}\right)^3} = \frac{8\pi\mu_0 \mu_B^2}{\left(0.91771a_0\right)^3} = 0.14803 \text{ eV}$$
 (13.524)

The  $CH_2$  bond dissociation energy,  $E_D(^{12}CH_2)$ , is given by the sum of the total energies of the CH radical and the hydrogen atom minus the sum of  $E_{T+osc}(^{12}CH_2)$  and E(magnetic):

$$E_{D}(^{12}CH_{2}) = E(^{12}CH) + E(H) - E_{T+osc}(^{12}CH_{2}) - E(magnetic)$$
 (13.525)

where  $E_T(^{12}CH)$  is given by the sum of the energies of the  $C2sp^3$  HO,  $E(C,2sp^3)$  given by 5 Eq. (13.428),  $E_D(H)$  given by Eq. (13.154), and the negative of the bond energy of  $^{12}CH$  given by Eq. (13.489):

$$E(^{12}CH) = -13.59844 \ eV - 14.63489 \ eV - 3.47 \ eV = -31.70333 \ eV \tag{13.526}$$

Thus, the  $^{12}CH_2$  bond dissociation energy,  $E_D(^{12}CH_2)$ , given by Eqs. (13.154), and (13.523-13.526) is

$$E_{D}(^{12}CH_{2}) = -(31.70333 \ eV + 13.59844 \ eV) - (E_{T+osc}(^{12}CH_{2}) + E(magnetic))$$

$$= -45.30177 \ eV - (-49.81948 \ eV + 0.14803 \ eV)$$

$$= 4.36968 \ eV$$
(13.527)

The experimental  $^{12}CH_2$  bond dissociation energy is [39]

$$E_D(^{12}CH_2) = 4.33064 \ eV \tag{13.528}$$

# 15 BOND ANGLE OF $^{12}CH_2$

The  $CH_2$  MO comprises a linear combination of two C-H-bond MOs. Each C-H-bond MO comprises the superposition of a  $H_2$ -type ellipsoidal MO and the  $C2sp^3$  HO with a relative charge density of 0.75 to 1.25; otherwise, the  $C2sp^3$  shell is unchanged. A bond is also possible between the two H atoms of the C-H bonds. Such H-H bonding would 20 decrease the C-H bond strength since electron density would be shifted from the C-H bonds to the H-H bond. Thus, the bond angle between the two C-H bonds is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal H atoms of the C-H bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the H-H ellipsoidal MO is

25 
$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_o}{2}}$$
 (13.529)

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{13.530}$$

The length of the semiminor axis of the prolate spheroidal H-H MO b=c is given by Eq. (13.62).

The bond angle of  $CH_2$  is derived by using the orbital composition and an energy 5 matching factor as in the case with  $NH_2$  and  $NH_3$ . Since the two  $H_2$ -type ellipsoidal MOs comprise 75% of the H electron density of  $H_2$  and the energy of each  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  HO; the component energies and the total energy  $E_T$  of the H-H bond are given by Eqs. (13.67-13.73) except that  $V_e$ , T, and  $V_m$  are corrected for the hybridization-energy-matching factor of 0.91771 given by Eq. (13.430). Substitution of Eq. (13.529) into Eq. (13.233) with the hybridization factor gives

$$0 = \begin{bmatrix} -e^{2} \\ 8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}} & \left[ (0.91771)^{-1} \left( \frac{3}{2} - \frac{3}{8} \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{4\pi\varepsilon_{o}a^{3}}{m_{e}}}}{\frac{2\hbar\sqrt{\frac{6.75e^{2}}{4\pi\varepsilon_{o}a^{3}}}}}{\frac{8\pi\varepsilon_{o}a^{3}}{0.5m_{p}}}} \right]$$

$$(13.531)$$

From the energy relationship given by Eq. (13.531) and the relationship between the axes given by Eqs. (13.529-13.530) and (13.62-13.63), the dimensions of the H-H MO can be 15 solved.

The most convenient way to solve Eq. (13.531) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 5.1500a_0 = 2.7253 \ X \ 10^{-10} \ m \tag{13.532}$$

Substitution of Eq. (13.532) into Eq. (13.529) gives

$$20 c' = 1.6047a_0 = 8.4916 X 10^{-11} m (13.533)$$

The internuclear distance given by multiplying Eq. (13.533) by two is

$$2c' = 3.2094a_0 = 1.6983 \ X \ 10^{-10} \ m \tag{13.534}$$

Substitution of Eqs. (13.532-13.533) into Eq. (13.62) gives

$$b = c = 4.8936a_0 = 2.5896 X 10^{-10} m ag{13.535}$$

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Substitution of Eqs. (13.532-13.533) into Eq. (13.63) gives

$$e = 0.3116 \tag{13.536}$$

Using,  $2c'_{H-H}$  (Eq. (13.534)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (13.531)), and  $2c'_{C-H}$  (Eq. (13.501)), the 5 internuclear distance of each C-H bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle  $\theta$  between the C-H bonds is

$$\theta = \cos^{-1}\left(\frac{2(2.09132)^2 - (3.2094)^2}{2(2.09132)^2}\right) = \cos^{-1}(-0.1775) = 100.22^{\circ}$$
 (13.537)

The experimental angle between the C-H bonds is [38]

$$\theta = 102.4^{\circ}$$
 (13.538)

The results of the determination of bond parameters of  $CH_2$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## 15 METHYL RADICAL (CH<sub>3</sub>)

The methyl radical  $CH_3$  is formed by the reaction of a hydrogen atom with a dihydrogen carbide radical:

$$CH_2 + H \rightarrow CH_3 \tag{13.539}$$

- $CH_3$  can be solved using the same principles as those used to solve and  $NH_3$  with the exception that the carbon 2s and 2p shells hybridize to form a single  $2sp^3$  shell as an energy minimum. Three diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with three carbon  $2sp^3$  hybridized orbitals (HOs) to form the MO of  $CH_3$ . The solution is very similar to that of  $CH_2$  except that there are three CH
  - bonds in  $CH_3$ .

## FORCE BALANCE OF CH3

 $CH_3$  comprises three chemical bonds between carbon and hydrogen atoms. Each C-H bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each H-atom electron forms a  $H_2$ -type ellipsoidal MO with an unpaired C-atom electrons. However, such a bond is not possible with the outer two C electrons in their ground state since the resulting  $H_2$ -type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon 2p shell which is not energetically stable, and only two electrons are unpaired. Thus, when bonding the carbon 2s and 2p shells hybridize to form a single  $2sp^3$  shell as an energy minimum. The electron configuration and the energy,  $E(C,2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422), and (13.428), respectively.

For each C-H bond, a  $C2sp^3$  electron combines with the H1s electron to form a molecular orbital. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , each of the three C-H-bond 15 MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the  $C2sp^3$  shell at the C atom whose nucleus serves as the other focus. The radius and the energy of the  $C2sp^3$  shell are unchanged with bond 20 formation. The central paramagnetic force due to spin of each C-H bond is provided by the spin-pairing force of the  $CH_3$  MO that has the symmetry of an s orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged.

The energies in the  $CH_3$  MO involve only each  $C2sp^3$  and each H1s electron with 25 the formation of each C-H bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. As in the cases with of OH,  $H_2O$ , NH,  $NH_2$ ,  $NH_3$ , CH, and  $CH_2$  the linear combination of each  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  HO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $C2sp^3$  HO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $CH_3$  MO must

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comprise three C-H bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO:

$$3[1 C2sp^3 + 0.75 H_2 MO] \rightarrow CH_3 MO$$
 (13.540)

5

The force balance of the  $CH_3$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.540) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each  $H_2$ -type10 ellipsoidal-MO component of the  $CH_3$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each C-H-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each C-H-bond MO. Since each of the three prolate spheroidal C-H-bond MOs comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $C2sp^3$  HO, the energy  $E(C,2sp^3)$  in Eq. (13.428) adds to that of the three corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_3$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_3$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ , T, and  $V_m$  are three times those of CH corresponding to the three C-H bonds. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C2sp^3$  HO and the energy of the  $C2sp^3$  shell must remain constant and equal to the  $E\left(C,2sp^3\right)$  given by Eq. (13.428), the total energy  $E_T\left(CH_3\right)$  of the  $CH_3$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C2sp^3$  HO and the three  $H_2$ -type ellipsoidal MOs that forms the  $CH_3$  MO as given by Eq. (13.540). Using Eq. (13.431),  $E_T\left(CH_3\right)$  is given by

$$E_{T}(CH_{3}) = E_{T} + E(C, 2sp^{3})$$

$$= -\frac{3e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \ eV$$
(13.541)

The three hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as a linear combination of three  $H_2$ -type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the C2sp3 HO-shell Coulombic 5 energy  $E_{Coulomb}(C,2sp^3)$  given by Eq. (13.435). To meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the  $C2sp^3$  HO, the electron energies in Eqs. (13.431), (13.495), and (13.541) were normalized by the ratio of 14.82575 eV, the magnitude of  $E_{Coulomb}(C,2sp^3)$  given by Eq. (13.425), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The 10 factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each C-H -bond MO under the influence of the proton and the C nucleus. Each C-H-bond MO comprises the same  $C2sp^3$  shell having its energy normalized to that of the Coulombic energy between the electron and a charge of +e at the carbon focus of the  $CH_3$  MO. Thus, the energy of the  $CH_3$  MO is also 15 given by the sum of that of the three  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus two times the Coulombic energy,  $E_{Coulomb}\left(H\right) = -13.605804 \; eV$ , of the two redundant +e's of the linear combination:

$$E_{T}(3H_{2}-2H) = -\frac{3e^{2}}{8\pi\varepsilon_{0}a_{0}} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] - 2E_{Coulomb}(H)$$

$$= 3\left( -31.63536831 \, eV \right) - 2\left( -13.605804 \, eV \right)$$

$$= -67.69450 \, eV$$
(13.542)

20  $E_T(CH_3)$  given by Eq. (13.541) is set equal to three times the energy of the  $H_2$ -type ellipsoidal MO minus two times the Coulombic energy of H given by Eq. (13.542):

$$E_T(CH_3) = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \ eV = -67.69450 \ eV$$
(13.543)

From the energy relationship given by Eq. (13.543) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_3$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.543) gives

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e53.05961$$
(13.544)

5 The most convenient way to solve Eq. (13.544) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.62893a_0 = 8.61990 \ X \ 10^{-11} \ m \tag{13.545}$$

Substitution of Eq. (13.545) into Eq. (13.60) gives

$$c' = 1.04209a_0 = 5.51450 \ X \ 10^{-11} \ m \tag{13.546}$$

10 The internuclear distance given by multiplying Eq. (13.546) by two is

$$2c' = 2.08418a_0 = 1.10290 \ X \ 10^{-10} \ m \tag{13.547}$$

The experimental bond distance is [38]

$$2c' = 1.079 X 10^{-10} m ag{13.548}$$

Substitution of Eqs. (13.545-13.546) into Eq. (13.62) gives

15 
$$b = c = 1.25198a_0 = 6.62518 \times 10^{-11} m$$
 (13.549)

Substitution of Eqs. (13.545-13.546) into Eq. (13.63) gives

$$e = 0.63974 \tag{13.550}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal

20 MO and the  $C2sp^3$  HO are given by Eqs. (13.84-13.95), (13.261-13.270), and (13.434-13.442). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{2sp^3} = 0.91771a_0$  is the radius of the  $C2sp^3$  shell. Substitution of Eqs. (13.545-13.546) into Eq. (13.261) gives

$$\theta' = 85.65^{\circ}$$
 (13.551)

25 Then, the angle  $\theta_{C2:p^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C2sp^3HO} = 180^{\circ} - 85.65^{\circ} = 94.35^{\circ} \tag{13.552}$$

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as shown in Figure 14. The angle  $\theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  radial vector given by Eqs. (13.442-13.443), (13.549), and (13.552) is

$$\theta_{H_2MO} = 46.96^{\circ} \tag{13.553}$$

5 Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.545), and (13.553) is

$$d_{H_2MO} = 1.11172a_0 = 5.88295 X 10^{-11} m (13.554)$$

The distance  $d_{C2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.546), and (13.554) is

$$d_{C2sp^3HO} = 0.06963a_0 = 3.68457 X 10^{-12} m ag{13.555}$$

As shown in Eq. (13.540), the uniform charge-density in the  $C2sp^3$  HO is increased by a factor of 0.25 and the H-atom density is decreased by a factor of 0.25 for by each C-H bond. Using the orbital composition of  $CH_3$  (Eq. (13.540)), the radii of 15  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C2sp^3 = 0.91771a_0$  (Eq. (10.424)) shells, and the parameters of the  $CH_3$  MO given by Eqs. (13.3-13.4), (13.545-13.547), and (13.549-13.555), the charge-density of the  $CH_3$  MO comprising the linear combination of three C-H-bond MOs is shown in Figure 17. Each C-H-bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO having the dimensional diagram shown in Figure 14.

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#### ENERGIES OF CH,

The energies of  $CH_3$  are three times those of CH and are given by the substitution of the semiprincipal axes (Eqs. (13.545-13.546) and (13.549)) into the energy equations Eq. (13.541) and (Eqs. (13.449-13.452)) that are multiplied by three:

25 
$$V_e = 3(0.91771) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -108.94944 \ eV$$
 (13.556)

$$V_p = \frac{3e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 39.16883 \ eV \tag{13.557}$$

$$T = 3(0.91771) \frac{\hbar^2}{2m_a a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 33.44213 \ eV$$
 (13.558)

$$V_m = 3(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -16.72107 \ eV$$
 (13.559)

$$E_{T}(CH_{3}) = -\frac{3e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \ eV = -67.69444 \ eV$$
(13.560)

5 where  $E_T(CH_3)$  is given by Eq. (13.541) which is reiteratively matched to Eq. (13.542) within five-significant-figure-round-off-error.

#### VIBRATION OF CH,

The vibrational energy levels of  $CH_3$  may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## 15 THE DOPPLER ENERGY TERMS OF 12CH,

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of methyl radical are the same as those of the corresponding hydrogen carbide radicals with the substitution of the methyl radical parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the 20 reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}} = 2.55577 \, X \, 10^{16} \, rad/s \tag{13.561}$$

where b is given by Eq. (13.549). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.55577 \, X \, 10^{16} \, rad \, / \, s = 16.82249 \, eV$$
 (13.562)

25 In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic

energy given by Eq. (13.562) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(16.82249 \ eV)}{m_e c^2}} = -0.25670 \ eV \tag{13.563}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH_3$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (13.563) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each C-H bond. Using  $\omega_e$  given by Eq. (13.458) for  $\overline{E}_{Kvib}$  of the transition state having three independent bonds,  $\overline{E}_{osc}^{\dagger}$  (12 $CH_3$ ) per bond is

$$\overline{E}'_{osc}\left(^{12}CH_{3}\right) = \overline{E}_{D} + \overline{E}_{Kvib} = \overline{E}_{D} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.564)

$$\overline{E}'_{asc}(^{12}CH_3) = -0.25670 \ eV + \frac{1}{2}(0.35532 \ eV) = -0.07904 \ eV$$
 (13.565)

Given that the vibration and reentrant oscillation is for three C-H bonds,  $\overline{E}_{csc}(^{12}CH_3)$ , is:

$$\overline{E}_{osc} \left( {}^{12}CH_3 \right) = 3 \left( \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) 
= 3 \left( -0.25670 \, eV + \frac{1}{2} (0.35532 \, eV) \right) 
= -0.23711 \, eV$$
(13.566)

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# TOTAL AND BOND ENERGIES OF 12CH3

 $E_{T+ose}(^{12}CH_3)$ , the total energy of the  $^{12}CH_3$  radical including the Doppler term, is given by the sum of  $E_T(CH_3)$  (Eq. (13.543)) and  $\overline{E}_{ose}(^{12}CH_3)$  given by Eq. (13.566):

$$E_{T+osc}(CH_3) = V_e + T + V_m + V_p + E(C, 2sp^3) + \overline{E}_{osc}(^{12}CH_3)$$

$$= E_T(CH_3) + \overline{E}_{osc}(^{12}CH_3)$$
(13.567)

$$E_{T+osc}(^{12}CH_3) = \begin{cases} \left(\frac{-3e^2}{8\pi\varepsilon_0c'} \left[ (0.91771) \left(2 - \frac{1}{2} \frac{a_0}{a}\right) \ln \frac{a+c'}{a-c'} - 1\right] - 14.63489 \ eV \right) \\ \left(-3 \left(31.63536831 \ eV \right) \sqrt{\frac{\frac{3}{4} \frac{e^2}{4\pi\varepsilon_0b^3}}{\frac{m_e}{m_ec^2}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}} \right) \end{cases}$$

$$= -67.69450 \ eV - 3 \left(0.25670 \ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right)$$

$$(13.568)$$

From Eqs. (13.564-13.568), the total energy of  $^{12}CH_3$  is

$$E_{T+ass}(^{12}CH_3) = -67.69450 \ eV + \overline{E}_{ass}(^{12}CH_3)$$

$$= -67.69450 \ eV - 3\left(0.25670 \ eV - \frac{1}{2}(0.35532 \ eV)\right)$$

$$= -67.93160 \ eV$$
(13.569)

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The  $CH_3$  bond dissociation energy,  $E_D(^{12}CH_3)$ , is given by the sum of the total energies of the  $CH_2$  radical and the hydrogen atom minus  $E_{T+asc}(^{12}CH_3)$ :

$$E_D(^{12}CH_3) = E(^{12}CH_2) + E(H) - E_{T+osc}(^{12}CH_3)$$
 (13.570)

where  $E_T(^{12}CH_2)$  is given by the sum of the energies of the  $C2sp^3$  HO,  $E(C,2sp^3)$  given by Eq. (13.428),  $2E_D(H)$  given by Eq. (13.154), and the negative of the bond energies of  $^{12}CH$  given by Eq. (13.489) and  $^{12}CH_2$  given by Eq. (13.528):

$$E(^{12}CH_2) = 2(-13.59844 \ eV) - 14.63489 \ eV - 3.47 \ eV - 4.33064 \ eV = -49.63241 \ eV$$
 (13.571)

Thus, the  $^{12}CH_3$  bond dissociation energy,  $E_D(^{12}CH_3)$ , given by Eqs. (13.154), and (13.569-13.571) is

$$E_{D}(^{12}CH_{3}) = -(-49.63241 \ eV - 13.59844 \ eV) - E_{T+ose}(^{12}CH_{3})$$

$$= -63.23085eV - (-67.93160 \ eV)$$

$$= 4.70075 \ eV$$
(13.572)

The experimental  ${}^{12}CH_3$  bond dissociation energy is [40]

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$$E_D(^{12}CH_3) = 4.72444 \ eV$$
 (13.573)

#### BOND ANGLE OF <sup>12</sup>CH,

Using,  $2c'_{H-H}$  (Eq. (13.534)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (13.531)), and  $2c'_{C-H}$ , the internuclear distance 5 of each C-H bond (Eq. (13.547)), the corresponding bond angle can be determined from the law of cosines. Using Eq. (13.537), the bond angle  $\theta$  between the C-H bonds is

$$\theta = \cos^{-1} \left( \frac{2(2.08418)^2 - (3.2094)^2}{2(2.08418)^2} \right)$$

$$= \cos^{-1} (-0.18560)$$

$$= 100.70^{\circ}$$
(13.574)

The  $CH_3$  radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance  $d_{origin-H}$  from the origin to the nucleus of a hydrogen atom given by Eqs. (13.534) and (13.412) is

$$d_{\text{origin-H}} = 1.85293a_0 \tag{13.575}$$

The height along the z-axis of the pyramid from the origin to C nucleus  $d_{height}$  given by Eqs. (13.414), (13.547), and (13.575) is

$$d_{height} = 0.95418a_0 \tag{13.576}$$

15 The angle  $\theta_{\nu}$  of each C-H bond from the z-axis given by Eqs. (13.416), (13.575), and (13.576) is

$$\theta_{\rm v} = 62.75^{\circ}$$
 (13.577)

The CH<sub>3</sub> MO shown in Figure 17 was rendered using these parameters.

The results of the determination of bond parameters of  $CH_3$  are given in Table 13.1.

20 The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

# METHANE MOLECULE (CH<sub>4</sub>)

25 The methane molecule  $CH_4$  is formed by the reaction of a hydrogen atom with a methyl radical:

$$CH_3 + H \rightarrow CH_4 \tag{13.578}$$

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 $CH_4$  can be solved using the same principles as those used to solve and  $CH_3$  wherein the carbon 2s and 2p shells hybridize to form a single  $2sp^3$  shell as an energy minimum. Four diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with four carbon  $2sp^3$  hybridized orbitals (HOs) to form the MO of  $CH_4$ . The solution is very similar to that of  $CH_3$  except that there are four CH bonds in  $CH_4$ . Methane is the simplest hydrocarbon that can be solved using the results for  $CH_3$ . From the solution of  $CH_2$  as well as  $CH_3$ , more complex hydrocarbons can be solved using these radical as basis elements with bonding between the  $C2sp^3$  hybridized carbons.

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### FORCE BALANCE OF CHA

 $CH_4$  comprises four chemical bonds between carbon and hydrogen atoms. Each C-H bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each H-atom electron forms a 15  $H_2$ -type ellipsoidal MO with an unpaired C-atom electrons. However, such a bond is not possible with the outer two C electrons in their ground state since the resulting  $H_2$ -type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon 2p shell which is not energetically stable, and only two electrons are unpaired. Thus, when bonding the carbon 2s and 2p shells hybridize to form a single  $2sp^3$  shell as an energy minimum. The electron configuration and the energy,  $E(C, 2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422), and (13.428), respectively.

For each C-H bond, a  $C2sp^3$  electron combines with the H1s electron to form a molecular orbital. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , each of the four C-H-bond 25 MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that can be solve as being continuous with the  $C2sp^3$  shell at the C atom whose nucleus serves as the other focus. The radius and the energy of the  $C2sp^3$  shell are

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unchanged with bond formation. The central paramagnetic force due to spin of each C-Hbond is provided by the spin-pairing force of the  $CH_4$  MO that has the symmetry of an sorbital that superimposes with the C2sp3 orbitals such that the corresponding angular momenta are unchanged.

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The energies in the  $CH_4$  MO involve only each  $C2sp^3$  and each H1s electron with the formation of each C-H bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. As in the cases with of OH,  $H_2O$ , NH,  $NH_2$ ,  $NH_3$ , CH,  $CH_2$ , and  $CH_3$  the  $CH_4$ , the  $CH_4$  MO must comprise four C-H bonds with each having 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO in a linear combination in order to 10 match potential, kinetic, and orbital energy relationships:

$$4\left[1 C2sp^{3} + 0.75 H_{2} MO\right] \rightarrow CH_{4} MO \tag{13.579}$$

The force balance of the CH<sub>4</sub> MO is determined by the boundary conditions that arise from 15 the linear combination of orbitals according to Eq. (13.579) and the energy matching condition between the hydrogen and C2sp3 HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each  $H_2$ -typeellipsoidal-MO component of the CH<sub>4</sub> MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each C-H-bond MO to each focus c' is 20 given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each C-H-bond MO. Since each of the four prolate spheroidal C-H-bond MOs comprises a  $H_2$ -type-25 ellipsoidal MO that transitions to the  $C2sp^3$  HO, the energy  $E(C,2sp^3)$  in Eq. (13.428) adds to that of the four corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the CH<sub>4</sub> MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_4$  MO are solved.

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The energy components of  $V_e$ ,  $V_p$ , T, and  $V_m$  are four times those of CH corresponding to the four C-H bonds. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C2sp^3$  HO and the energy of the  $C2sp^3$  shell must remain constant and equal to the  $E(C,2sp^3)$  given by Eq. (13.428), the total energy  $E_T(CH_4)$  of the  $CH_4$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C2sp^3$  HO and the four  $H_2$ -type ellipsoidal MOs that forms the  $CH_4$  MO as given by Eq. (13.579). Using Eq. (13.431),  $E_T(CH_4)$  is given by

$$E_{T}(CH_{4}) = E_{T} + E(C, 2sp^{3})$$

$$= -\frac{4e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \ eV$$
(13.580)

The four hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as 10 a linear combination of four  $H_2$ -type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the C2sp3 HO-shell Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  given by Eq. (13.435). To meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the  $C2sp^3$  HO, the electron energies in Eqs. (13.431), (13.495), (13.541), and (13.580) were normalized by the ratio of 14.82575 eV, the 15 magnitude of  $E_{Coulomb}(C, 2sp^3)$  given by Eq. (13.425), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each C-H-bond MO under the influence of the proton and the C nucleus. Each C-H-bond MO comprises the same  $C2sp^3$  shell 20 having its energy normalized to that of the Coulombic energy between the electron and a charge of +e at the carbon focus of the CH<sub>4</sub> MO. Thus, the energy of the CH<sub>4</sub> MO is also given by the sum of that of the four  $H_2$ -type ellipsoidal MOs given by Eq. (11.212) minus three times the Coulombic energy,  $E_{Coulomb}(H) = -13.605804 \, eV$ , of the three redundant +e's of the linear combination:

$$E_{T}(4H_{2}-3H) = -\frac{4e^{2}}{8\pi\varepsilon_{0}a_{0}} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] - 3E_{Coulomb}(H)$$

$$= 4\left( -31.63536831 \, eV \right) - 3\left( -13.605804 \, eV \right)$$

$$= -85.72406 \, eV$$
(13.581)

 $E_T(CH_4)$  given by Eq. (13.580) is set equal to four times the energy of the  $H_2$ -type ellipsoidal MO minus three times the Coulombic energy of H given by Eq. (13.581):

$$E_{T}(CH_{4}) = -\frac{4e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.63489 \ eV = -85.72406 \ eV$$
(13.582)

From the energy relationship given by Eq. (13.582) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_4$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.543) gives

$$\frac{4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e71.08917$$
(13.583)

10 The most convenient way to solve Eq. (13.583) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.62340a_0 = 8.59066 \ X \ 10^{-11} \ m \tag{13.584}$$

Substitution of Eq. (13.584) into Eq. (13.60) gives

$$c' = 1.04032a_0 = 5.50514 \ X \ 10^{-11} \ m \tag{13.585}$$

15 The internuclear distance given by multiplying Eq. (13.585) by two is

$$2c' = 2.08064a_0 = 1.10103 \ X \ 10^{-10} \ m$$
 (13.586)

The experimental bond distance is [41]

$$2c' = 1.087 X 10^{-10} m ag{13.587}$$

Substitution of Eqs. (13.584-13.585) into Eq. (13.62) gives

20 
$$b = c = 1.24626a_0 = 6.59492 \times 10^{-11} m$$
 (13.588)

Substitution of Eqs. (13.584-13.585) into Eq. (13.63) gives

$$e = 0.64083 \tag{13.589}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each  $H_2$ type ellipsoidal MO. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal

MO and the  $C2sp^3$  HO in the absence of the other three are given by Eqs. (13.84-13.95), (13.261-13.270), (13.434-13.442), and (13.551-13.555). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{2sp^3} = 0.91771a_0$  is the radius of the  $C2sp^3$  shell. Substitution of Eqs. (13.584-13.585) into Eq. (13.261) gives

5 
$$\theta' = 86.20^{\circ}$$
 (13.590)

Then, the angle  $\theta_{C2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C2:p^3HO} = 180^{\circ} - 86.20^{\circ} = 93.80^{\circ} \tag{13.591}$$

as shown in Figure 14. The angle  $\theta_{H_2MO}$  between the internuclear axis and the point of 10 intersection of each  $H_2$ -type ellipsoidal MO with the  $C2sp^3$  radial vector given by Eqs. (13.442-13.443), (13.588), and (13.591) is

$$\theta_{H_2MO} = 47.29^{\circ}$$
 (13.592)

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.584), and (13.592) is

$$d_{H_2MO} = 1.10121a_0 = 5.82734 \ X \ 10^{-11} \ m \tag{13.593}$$

The distance  $d_{C2,p^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.585), and (13.593) is

$$d_{C2sp^3HO} = 0.06089a_0 = 3.22208 X 10^{-12} m ag{13.594}$$

The  $H_2$ -type ellipsoidal MOs do not actually directly contact the  $C2sp^3$  HO. As discussed in the Force Balance of  $H_2O$  section, with the addition of the fourth C-H bond, the  $H_2$ -type ellipsoidal MOs may linearly combine to form a continuous two-dimensional surface of equipotential equivalent to that of the MOs if they did contact the  $C2sp^3$  HO. However, Eqs. (13.579-13.580) must hold based on conservation of momentum and the potential, kinetic, and total energy relationships. In order that there is current continuity given the constraints of Eqs. (13.579-13.580), the existence of a self-contained, continuous-current, linear-combination of the  $H_2$ -type ellipsoidal MOs requires that electrons are divisible between the combination  $H_2$ -type MO and the  $C2sp^3$  HO. This is not possible. Thus, at the points of intersection of the  $H_2$ -type MOs of methane, symmetry, electron

indivisibility, current continuity, and conservation of energy and angular momentum require that the current between the  $C2sp^3$  shell and points of mutual contact is projected onto and flows along the radial vector to the surface of  $C2sp^3$  shell. This current designated the bisector current (BC) meets the  $C2sp^3$  surface and does not travel to distances shorter than its radius. Moreover, an energy minimum is obtained when the H-atom charge-density of each C-H-bond MO is decreased by a factor of 0.25 with a corresponding 0.25 increase in that of the three other C-H-bond MOs. In this case, the angular momentum components of the transferred current mutually cancel. The geometry of the equivalent bonds is tetrahedral. The symmetry point group is  $T_d$ . This geometry is equivalent to the indistinguishable bonds positioned uniformly on a spherical surface or also at the apexes of a cube. The predicted angle  $\theta$  between the C-H bonds is

$$\theta = 109.5^{\circ}$$
 (13.595)

The experimental bond angle is [41]

$$\theta = 109.5^{\circ}$$
 (13.596)

15 The polar angle  $\phi$  at which the  $H_2$ -type ellipsoidal MOs intersect is given by the bisector of the angle  $\theta$  between the C-H bonds:

$$\phi = \frac{109.5}{2} = 54.75^{\circ} \tag{13.597}$$

With the carbon nucleus defined as the origin and one of the C-H bonds defined as the positive x-axis, the polar-coordinate angle of the intersection occurs at

20 
$$\phi' = 54.75^{\circ} + 180^{\circ} = 234.57^{\circ}$$
 (13.598)

The polar radius  $r_i$  at this angle is given by Eqs. (13.84-13.85):

$$r_{i} = \left(a - c'\right) \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a}\cos\phi'}$$
 (13.599)

Substitution of Eqs. (13.584-13.585) and (13.589) into Eq. (13.599) gives

$$r_i = 1.52223a_0 = 8.05530 X 10^{-11} m ag{13.600}$$

Using the orbital composition of  $CH_4$  (Eq. (13.579)), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C2sp^3 = 0.91771a_0$  (Eq. (10.424)) shells, and the parameters of the  $CH_4$  MO given by Eqs. (13.3-13.4), (13.584-13.586), and (13.588-13.600), the charge-density of the  $CH_4$  MO comprising the linear combination of four C-H-bond MOs is shown in

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Figure 18. Each C-H-bond MO having the dimensional diagram shown in Figure 14 comprises a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO according to Eq. (13.579). But, based on the  $T_d$  symmetry of the  $H_2$ -type MOs, the charge is distributed 1:1 between the  $H_2$ -type MOs and the  $C2sp^3$  shell.

5

### ENERGIES OF CH4

The energies of  $CH_4$  are four times those of CH and are given by the substitution of the semiprincipal axes (Eqs. (13.584-13.585) and (13.588)) into the energy equations Eq. (13.580) and (Eqs. (13.449-13.452)) that are multiplied by four:

10 
$$V_e = 4(0.91771) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -145.86691 \ eV \tag{13.601}$$

$$V_p = \frac{4e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 52.31390 \ eV \tag{13.602}$$

$$T = 4(0.91771) \frac{\hbar^2}{2m \cdot a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 44.92637 \ eV$$
 (13.603)

$$V_m = 4(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -22.46318 \text{ eV}$$
 (13.604)

$$E_{T}(CH_{4}) = -\frac{4e^{2}}{8\pi\varepsilon_{0}c^{4}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c^{4}}{a - c^{4}} - 1 \right] - 14.63489 \ eV = -85.72472 \ eV$$

15 (13.605)

where  $E_T(CH_4)$  is given by Eq. (13.580) which is reiteratively matched to Eq. (13.581) within five-significant-figure round-off error.

#### VIBRATION OF CH.

20 The vibrational energy levels of  $CH_4$  may be solved as four equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF 12CH4

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of methane are the same as those of OH, CH,  $CH_2$ , and  $CH_3$  with the substitution of the methane parameters. Using Eqs. 5 (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}} = 2.57338 \, X \, 10^{16} \, rad/s \tag{13.606}$$

where b is given by Eq. (13.588). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

10 
$$\overline{E}_{\kappa} = \hbar \omega = \hbar 2.57338 \, X \, 10^{16} \, rad / s = 16.93841 \, eV$$
 (13.607)

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.607) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the four bonds for the reentrant orbit:

15 
$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(16.93841 \ eV)}{m_e c^2}} = -0.25758 \ eV$$
 (13.608)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH_4$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding 20 energies,  $\overline{E}_D$  given by Eq. (13.608) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each C-H bond. Using  $\omega_e$  given by Eq. (13.458) for  $\overline{E}_{Kvib}$  of the transition state having four independent bonds,  $\overline{E}'_{osc}(^{12}CH_4)$  per bond is

$$\overline{E}'_{asc}(^{12}CH_4) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.609)

$$\overline{E}'_{osc}(^{12}CH_4) = -0.25758 \ eV + \frac{1}{2}(0.35532 \ eV) = -0.07992 \ eV$$
 (13.610)

The reentrant orbit for the binding of a hydrogen atom to a  $CH_3$  radical involves four C-H bonds. Since the vibration and reentrant oscillation is along four bonds,  $\overline{E}_{osc}$  for  $^{12}CH_4$ ,  $\overline{E}_{osc}$  ( $^{12}CH_4$ ), is:

$$\overline{E}_{osc}(^{12}CH_4) = 4\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$= 4\left(-0.25758 \, eV + \frac{1}{2}(0.35532 \, eV)\right)$$

$$= -0.31967 \, eV$$
(13.611)

5

### TOTAL AND BOND ENERGIES OF 12CH4

 $E_{T+ose}(^{12}CH_4)$ , the total energy of the  $^{12}CH_4$  radical including the Doppler term, is given by the sum of  $E_T(CH_4)$  (Eq. (13.582)) and  $\overline{E}_{ose}(^{12}CH_4)$  given by Eq. (13.611):

$$E_{T+asc}(CH_4) = V_e + T + V_m + V_p + E(C, 2sp^3) + \overline{E}_{osc}(^{12}CH_4)$$

$$= E_T(CH_4) + \overline{E}_{osc}(^{12}CH_4)$$
(13.612)

$$E_{T+acc}(^{12}CH_{4}) = \begin{cases} \left(\frac{-4e^{2}}{8\pi\varepsilon_{0}c'}\right[(0.91771)\left(2-\frac{1}{2}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV) \\ -4\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^{2}}{4\pi\varepsilon_{0}b^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}}\right) \\ = -85.72406\ eV - 4\left(0.25758\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{cases}$$

10

(13.613)

From Eqs. (13.609-13.613), the total energy of  $^{12}CH_4$  is

$$\begin{split} E_{T+osc}\left(^{12}CH_{4}\right) &= -85.72406 \ eV + \overline{E}_{osc}\left(^{12}CH_{4}\right) \\ &= -85.72406 \ eV - 4\bigg(0.25758 \ eV - \frac{1}{2}\big(0.35532 \ eV\big)\bigg) \\ &= -86.04373 \ eV \end{split} \tag{13.614}$$

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

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The  $CH_4$  bond dissociation energy,  $E_D(^{12}CH_4)$ , is given by the sum of the total energies of the  $CH_3$  radical and the hydrogen atom minus  $E_{T+osc}(^{12}CH_4)$ :

$$E_{D}(^{12}CH_{4}) = E(^{12}CH_{3}) + E(H) - E_{T+osc}(^{12}CH_{4})$$
(13.615)

where  $E_T(^{12}CH_3)$  is given by the sum of the energies of the  $C2sp^3$  HO,  $E(C,2sp^3)$  given 5 by Eq. (13.428),  $3E_D(H)$  given by Eq. (13.154), and the negative of the bond energies of  $^{12}CH$  given by Eq. (13.489),  $^{12}CH_2$  given by Eq. (13.528), and  $^{12}CH_3$  given by Eq. (13.573):

$$E(^{12}CH_3) = \begin{pmatrix} 3(-13.59844 \ eV) - 14.63489 \ eV \\ -3.47 \ eV - 4.33064 \ eV - 4.72444 \ eV \end{pmatrix} = -67.95529 \ eV$$
 (13.616)

Thus, the  $^{12}CH_4$  bond dissociation energy,  $E_D(^{12}CH_4)$ , given by Eqs. (13.154), and (13.614-13.616) is

$$E_{D}(^{12}CH_{4}) = -(67.95529 \ eV + 13.59844 \ eV) - E_{T+osc}(^{12}CH_{4})$$

$$= -81.55373 \ eV - (-86.04373 \ eV)$$

$$= 4.4900 \ eV$$
(13.617)

The experimental <sup>12</sup>CH<sub>4</sub> bond dissociation energy is [40]

$$E_D(^{12}CH_4) = 4.48464 \ eV \tag{13.618}$$

The results of the determination of bond parameters of  $CH_4$  are given in Table 13.1.

15 The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

#### NITROGEN MOLECULE

10

20 The nitrogen molecule can be formed by the reaction of two nitrogen atoms:

$$N + N \to N_2 \tag{13.619}$$

The bond in the nitrogen molecule comprises a  $H_2$ -type molecular orbital (MO) with two paired electrons. The force balance equation and radius  $r_7$  of the 2p shell of N is derived in the Seven-Electron Atoms section. With the formation of the  $H_2$ -type MO by the 25 contribution of a 2p electron from each N atom, a diamagnetic force arises between the

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remaining 2p electrons and the  $H_2$ -type MO. This force from each N causes the  $H_2$ -type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining 2p electrons of each N decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $N_2$  is  $1s_1^21s_2^22s_1^22s_2^22p_1^22p_2^2\sigma_{1,2}^2$  where the subscript designates the N atom, 1 or 2,  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

Nitrogen is predicted to be diamagnetic in agreement with observations [42].

# FORCE BALANCE OF THE 2p SHELL OF THE NITROGEN ATOMS OF THE NITROGEN MOLECULE

For each N atom, force balance for the outermost 2p electron of  $N_2$  (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other 2p-shell as well as the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-20 Electron Atoms section. The central Coulomb force on the outer-most 2p shell electron of  $N_2$  (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with

the appropriate charge and radius:

$$\mathbf{F}_{els} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} \mathbf{i}_r \tag{13.621}$$

for  $r > r_5$ . The 2p shell possess an external electric field given by Eq. (10.92) for  $r > r_6$ . The energy is minimized with conservation of angular momentum. This condition is met 5 when the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the p-orbital contribution is the same as that of the reactant nitrogen atoms given by Eq. (10.136) with  $r_6$  replacing  $r_7$ :

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right) \frac{\hbar^2}{4m_e r_e^2 r_3} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}} = -\frac{\hbar^2}{12m_e r_e^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_{\mathbf{r}}$$
(13.622)

And,  $F_{mag 2}$  corresponding to the conserved orbital angular momentum of the three orbitals is given by Eq. (10.89):

10 
$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
 (13.623)

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_6$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is:

$$\mathbf{F}_{diamognetic\ 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10\sqrt{s(s+1)} \mathbf{i_r}$$
 (13.624)

In addition, the contribution of a 2p electron from each N atom in the formation of the  $\sigma$  MO gives rise to a paramagnetic force on the remaining two 2p electrons that pair. The force,  $\mathbf{F}_{mog 3}$ , follows from Eq. (10.11) wherein the two radii are equal to  $r_6$  and the direction is positive, central:

$$\mathbf{F}_{mag \ 3} = \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}}$$
 (13.625)

20  $\mathbf{F}_{mag \ 3}$  is present in additional diatomic molecules where its contribution minimizes the energy. This AO spin-pairing force reduces the radius directly to reduce the energy, and it can also cancel the contribution of the corresponding electron to  $\mathbf{F}_{diamagnetic}$  to further reduce the energy.

The radius of the 2p shell is calculated by equating the outward centrifugal force to 25 the sum of the electric (Eq. (13.621)) and diamagnetic (Eqs. (13.622) and (13.624)), and paramagnetic (Eqs. (13.623) and (13.625)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \begin{pmatrix}
\frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{\hbar^2}{12m_e r_6^2 r_3} \sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} \\
- \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)}
\end{pmatrix}$$
(13.626)

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.626) gives:

$$\frac{\hbar^{2}}{m_{e}r_{6}^{3}} - \frac{\hbar^{2}}{4m_{e}r_{6}^{3}} \sqrt{\frac{3}{4}} = \frac{(Z-5)e^{2}}{4\pi\varepsilon_{0}r_{6}^{2}} - \frac{\hbar^{2}}{12m_{e}r_{6}^{2}r_{3}} \sqrt{\frac{3}{4}} + \frac{3\hbar^{2}}{Zm_{e}r_{6}^{2}r_{3}} \sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_{3}\hbar^{2}}{r_{6}^{4}m_{e}} 10\sqrt{\frac{3}{4}}$$
(13.627)

5 The quadratic equation corresponding to Eq. (13.627) is

$$r_{6}^{2} - \frac{\frac{\hbar^{2}}{m_{e}} \left(1 - \frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z - 5)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} r_{6} - \frac{\frac{\hbar^{2}}{m_{e}} \left[\frac{Z - 6}{Z - 5}\right] \left(1 - \frac{\sqrt{2}}{2}\right)r_{3}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z - 5)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} = 0$$
(13.628)

The solution of Eq. (13.628) using the quadratic formula is:

$$a_{0}\left(1-\frac{\sqrt{3}}{8}\right) = \left((Z-5)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{2} + \frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-5)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

$$r_{6} = \frac{20\sqrt{3}\left(\frac{Z-6}{Z-5}\right)\left(1-\frac{\sqrt{2}}{2}\right)r_{3}}{2r_{3}}$$

$$(13.629)$$

 $r_{2}$  in units of  $a_{0}$ 

10 The positive root of Eq. (13.629) must be taken in order that  $r_6 > 0$ . Substitution of

$$\frac{r_3}{a_0} = 0.69385$$
 (Eq. (10.62) with  $Z = 7$ ) into Eq. (13.629) gives
$$r_c = 0.78402a_0 \tag{13.630}$$

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# ENERGIES OF THE 2p SHELL OF THE NITROGEN ATOMS OF THE NITROGEN MOLECULE

The central forces on the 2p shell of each N are increased with the formation of the  $\sigma$  MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the two N atoms at the new radius are calculated and added to the energy of the  $\sigma$  MO to give the total energy of  $N_2$ . Then, the bond energy is determined from the total  $N_2$  energy.

The radius  $r_7$  of each nitrogen atom before bonding is given by Eq. (10.142):

$$r_2 = 0.93084a_0 \tag{13.631}$$

10 Using the initial radius  $r_7$  of each N atom and the final radius  $r_6$  of the N2p shell of  $N_2$  (Eq. (13.630)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(N_2, 2p)$  of the Coulombic energy change of the N2p electrons of both atoms is determined using Eq. (10.102):

$$E_{T}(N_{2}, 2p) = -2\sum_{n=4}^{5} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{6}} - \frac{1}{r_{7}}\right)$$

$$= -2(13.60580 \text{ eV})(0.20118)(2+3)$$

$$= -27.37174 \text{ eV}$$
(13.632)

15

### FORCE BALANCE OF THE $\sigma$ MO OF THE NITROGEN MOLECULE

The 2p shell gives rise to two diamagnetic forces on the  $\sigma$  MO. As given for the hydrogen molecule in the Hydrogen-Type Molecules section, the  $\sigma$  MO comprises two electrons,  $\sigma$  electron 1 and  $\sigma$  electron 2, that are bound at  $\xi=0$  as a equipotential prolate spheroidal MO by the central Coulombic field due to the nitrogen atoms at the foci and the spin pairing force on  $\sigma$  electron 2 due to  $\sigma$  electron 1 that initially has smaller semiprincipal axes. The spin-pairing force given in Eq. (11.200) is equal to one half the centrifugal force of the two electrons. The spin-pairing electron of the  $\sigma$  MO is also repelled by the remaining 2p electrons of each N according to Lenz law, and the force is based on the total number of these electrons  $n_e$  that interact with the binding  $\sigma$ -MO electron. This diamagnetic force  $\mathbf{F}_{diamagneticMO1}$  is of the same form as the molecular spin-pairing force but in the opposite direction. The force follows from the derivations of Eqs. (10.219) and (11.200) which gives:

$$\mathbf{F}_{diamogneticMO1} = \frac{n_e \hbar^2}{4m_e a^2 b^2} D\mathbf{i}_{\xi}$$
 (13.633)

In addition, there is a relativistically corrected Lorentzian force  $\mathbf{F}_{diamagneticMO2}$  on the pairing electron of the  $\sigma$  MO that follows from Eqs. (7.15) and (11.200):

$$\mathbf{F}_{diamogneticMO2} = \frac{1}{Z} \frac{|L|\hbar}{2m_e a^2 b^2} D\mathbf{i}_{g}$$
 (13.634)

5 where |L| is the magnitude of the angular momentum of each N atom at a focus that is the source of the diamagnetism at the  $\sigma$ -MO.

The force balance equation for the  $\sigma$ -MO of the nitrogen molecule given by Eq. (11.200) and Eqs. (13.633-13.634) with  $n_e = 2$  and  $|L| = \hbar$  is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi \varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.635}$$

10 
$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D - \frac{1}{Z} \frac{\hbar^2}{2m_e a^2 b^2} D$$
 (13.636)

$$\left(2 + \frac{1}{Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi \varepsilon_0 a b^2} D \tag{13.637}$$

$$a = \left(2 + \frac{1}{Z}\right)a_0 \tag{13.638}$$

Substitution of Z = 7 into Eq. (13.638) gives

$$a = 2.14286a_0 = 1.13395 \ X \ 10^{-10} \ m \tag{13.639}$$

15 Substitution of Eq. (13.639) into Eq. (11.79) is

$$c' = 1.03510a_0 = 5.47750 \ X \ 10^{-11} \ m \tag{13.640}$$

The internuclear distance given by multiplying Eq. (13.640) by two is

$$2c' = 2.07020a_0 = 1.09550 \ X \ 10^{-10} \ m \tag{13.641}$$

The experimental bond distance from Ref. [28] and Ref. [43] is

$$2c' = 1.09769 X 10^{-10} m ag{13.642}$$

$$2c' = 1.094 X 10^{-10} m ag{13.643}$$

Substitution of Eqs. (13.639-13.640) into Eq. (11.80) is

$$b = c = 1.87628a_0 = 9.92882 \ X \ 10^{-11} \ m \tag{13.644}$$

Substitution of Eqs. (13.639-13.640) into Eq. (11.67) is

$$25 e = 0.48305 (13.645)$$

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Using the electron configuration of  $N_2$  (Eq. (13.620)), the radii of the  $N1s = 0.14605a_0$  (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)), and  $N2p = 0.78402a_0$  (Eq. (13.630)) shells and the parameters of the  $\sigma$  MO of  $N_2$  given by Eqs. (13.3-13.4), (13.639-13.641), and (13.644-13.645), the dimensional diagram and charge-density of the  $N_2$  MO are shown in Figures 19 and 20, respectively.

Despite the predictions of standard quantum mechanics that preclude the imaging of a molecular orbital, the full three-dimensional structure of the outer molecular orbital of  $N_2$  has been recently tomographically reconstructed [44]. The charge-density surface observed is consistent with that shown in Figure 20. This result constitutes direct evidence that electrons are not point-particle probability waves that have no form until they are "collapsed to a point" by measurement. Rather they are physical, two-dimensional equipotential charge density surfaces.

# SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE 15 NITROGEN MOLECULE

The energies of the  $N_2$   $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (13.639-13.640) and (13.644)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$ :

$$V_{e} = \frac{-2e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} = -27.70586 \, eV$$
 (13.646)

$$V_{p} = \frac{e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} = 13.14446 \, eV \tag{13.647}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 6.46470 \ eV$$
 (13.648)

$$V_{m} = \frac{-\hbar^{2}}{4m_{c}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -3.23235 \ eV$$
 (13.649)

$$E_T = V_e + T + V_m + V_n \tag{13.650}$$

Substitution of Eqs. (11.79) and (13.646-13.649) into Eq. (13.650) gives

20

$$E_{T}(N_{2},\sigma) = \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left( \left(2 - \frac{1}{2} \frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1 \right) = -11.32906 \ eV$$
 (13.651)

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where  $E_T(N_2, \sigma)$  is the total energy of the  $\sigma$  MO of  $N_2$ . The sum,  $E_T(N_2)$ , of  $E_T(N_2, 2p)$ , the 2p (AO) contribution given by Eq. (13.632), and  $E_T(N_2, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.651) is:

$$E_{T}(N_{2}) = E_{T}(N_{2}, 2p) + E_{T}(N_{2}, \sigma)$$

$$= -27.37174 \ eV - 11.32906 \ eV$$

$$= -38.70080 \ eV$$
(13.652)

5

#### VIBRATION OF N,

The vibrational energy levels of  $N_2$  may be solved by determining the Morse potential curve from the energy relationships for the transition from two N atoms whose parameters are given by Eqs. (10.134-10.143) to the two N atoms whose parameter  $r_6$  is given by Eq. (13.630) and the  $\sigma$  MO whose parameters are given by Eqs. (13.639-13.641) and (13.644-13.645). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE NITROGEN MOLECULE

The equations of the radiation reaction force of nitrogen are the same as those of  $H_2$  with the substitution of the nitrogen parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{e^2}{4\pi\varepsilon_0 a^3}} = 1.31794 \, X \, 10^{16} \, rad/s \tag{13.653}$$

where a is given by Eq. (13.639). The kinetic energy,  $E_{\kappa}$ , is given by Planck's equation (Eq. (11.127)):

25 
$$\overline{E}_K = \hbar\omega = \hbar 1.31794 \, X \, 10^{16} \, rad \, / s = 8.67490 \, eV$$
 (13.654)

In Eq. (11.181), substitution of  $E_T(N_2)$  for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.654) for  $\overline{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -38.70080 \ eV \sqrt{\frac{2e(8.67490 \ eV)}{m_e c^2}} = -0.22550 \ eV \tag{13.655}$$

5 In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $N_2$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (13.655) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the 10 vibrational energy. Using the experimental  $N_2$   $\omega_e$  of 2358.57 cm<sup>-1</sup> (0.29243 eV) [28] for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{osc}(N_2)$  is

$$\overline{E}_{osc}(N_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.656)

$$\overline{E}_{osc}(N_2) = -0.22550 \ eV + \frac{1}{2}(0.29243 \ eV) = -0.07929 \ eV$$
 (13.657)

#### 15 TOTAL AND BOND ENERGIES OF THE NITROGEN MOLECULE

 $E_{T+osc}(N_2)$ , the total energy of  $N_2$  including the Doppler term, is given by the sum of  $E_T(N_2)$  (Eq. (13.652)) and  $\overline{E}_{osc}(N_2)$  given by Eq. (13.657):

$$E_{T+osc}(N_2) = V_e + T + V_m + V_p + E_T(N_2, 2p) + \overline{E}_{osc}(N_2)$$

$$= E_T(N_2, \sigma) + E_T(N_2, 2p) + \overline{E}_{osc}(N_2)$$

$$= E_T(N_2) + \overline{E}_{osc}(N_2)$$
(13.658)

$$E_{T+osc}(N_{2}) = \begin{cases} \left(\frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left(2 - \frac{1}{2} \frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1\right) - 2\sum_{n=4}^{5} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{6}} - \frac{1}{r_{7}}\right) \right) \\ \left(1 + \sqrt{\frac{e^{2}}{4\pi\varepsilon_{0}a^{3}}} \frac{1}{m_{e}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \\ = -38.70080 \ eV - 0.22550 \ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{cases}$$

$$(13.659)$$

From Eqs. (13.656-13.659), the total energy of the  $N_2$  MO is

$$E_{T+ase}(N_2) = -38.70080 \ eV + \overline{E}_{ase}(N_2)$$

$$= -38.70080 \ eV - 0.22550 \ eV + \frac{1}{2}(0.29243 \ eV)$$

$$= -38.78009 \ eV$$
(13.660)

where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

The  $N_2$  bond dissociation energy,  $E_D(N_2)$ , is given by the difference in the total energies of the two N atoms and  $E_{T+asc}(N_2)$ :

$$E_{D}(N_{2}) = 2E(N) - E_{T+osc}(N_{2})$$
(13.661)

where the energy of a nitrogen atom is [6]

$$E(N) = -14.53414 \ eV \tag{13.662}$$

10 Thus, the  $N_2$  bond dissociation energy,  $E_D(N_2)$ , given by Eqs. (13.660-13.662) is

$$E_D(N_2) = -2(14.53414 \ eV) - E_{T+osc}(N_2)$$

$$= -29.06828 \ eV - (-38.78009 \ eV)$$

$$= 9.71181 \ eV$$
(13.663)

The experimental  $N_2$  bond dissociation energy from Ref. [43] and Ref. [45] is

$$E_D(N_2) = 9.756 \, eV$$
 (13.664)

$$E_D(N_2) = 9.764 \ eV \tag{13.665}$$

15 The results of the determination of bond parameters of  $N_2$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations

containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

#### **OXYGEN MOLECULE**

5 The oxygen molecule can be formed by the reaction of two oxygen atoms:

$$O+O \to O_2 \tag{13.666}$$

The bond in the oxygen molecule comprises a  $H_2$ -type molecular orbital (MO) with two paired electrons. The force balance equation and radius  $r_8$  of the 2p shell of O is derived in the Eight-Electron Atoms section. With the formation of the  $H_2$ -type MO by the contribution of a 2p electron from each O atom, a diamagnetic force arises between the remaining 2p electrons and the  $H_2$ -type MO. This force from each O causes the  $H_2$ -type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining 2p electrons of each O decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $O_2$  is  $1s_1^21s_2^22s_1^22s_2^22p_1^32p_2^3\sigma_{1,2}^2$  where the subscript designates the O atom, 1 or 2,  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

$$\begin{array}{c|cccc}
 & \sigma & \text{state} \\
 & \uparrow \downarrow \\
\hline
 & \uparrow \\
\hline
 & 0 & 1
\end{array}$$

$$\begin{array}{c|ccccc}
 & 2p & \text{state} \\
\hline
 & \uparrow \downarrow \\
\hline
 & 1 & 0 & 1
\end{array}$$

$$\begin{array}{c|ccccc}
 & 2s & \text{state} \\
\hline
 & \uparrow \downarrow \\
\hline
 & 1s & \text{state} \\
\hline
 & \uparrow \downarrow \\
\hline
 & O1 & O2
\end{array}$$
(13.667)

Oxygen is predicted to be paramagnetic in agreement with observations [42].

# FORCE BALANCE OF THE 2p SHELL OF THE OXYGEN ATOMS OF THE OXYGEN MOLECULE

5 For each O atom, force balance for the outermost 2p electron of  $O_2$  (electron 7) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 7 and the other 2p-shell as well as the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most 2p shell electron of  $O_2$  (electron 7) due to the nucleus and the inner six electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-6)e^2}{4\pi\varepsilon_0 r_1^2} \mathbf{i}_{\mathbf{r}} \tag{13.668}$$

for  $r > r_6$ . The 2p shell possess an external electric field given by Eq. (10.92) for  $r > r_7$ . The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces are the same as those of the reactant oxygen atoms with  $r_7$  replacing  $r_8$ . The diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the p-orbital contributions is given by Eq. (10.156):

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3} + \frac{2}{3}\right) \frac{\hbar^2}{4m_e r_1^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{3\hbar^2}{12m_e r_1^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r$$
 (13.669)

And,  $\mathbf{F}_{mag 2}$  corresponding to the conserved spin and orbital angular momentum given by Eq. 20 (10.157) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{2\hbar^2}{m_e r_1^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
 (13.670)

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_7$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is:

25 
$$\mathbf{F}_{diamognetic\ 2} = -\left[\frac{Z-7}{Z-6}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_1^4} 10\sqrt{s(s+1)} \mathbf{i}_r$$
 (13.671)

The radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.688)) and diamagnetic (Eqs. (13.669) and (13.671)), and

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paramagnetic (Eq. (13.670)) forces as follows:

$$\frac{m_e v_{\gamma}^2}{r_{\gamma}} = \begin{pmatrix}
\frac{(Z-6)e^2}{4\pi\varepsilon_0 r_{\gamma}^2} - \frac{3\hbar^2}{12m_e r_{\gamma}^2 r_3} \sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_{\gamma}^2 r_3} \sqrt{s(s+1)} \\
-\left[\frac{Z-7}{Z-6}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_{\gamma}\hbar^2}{r_{\gamma}^4 m_e} 10\sqrt{s(s+1)}$$
(13.672)

Substitution of  $v_7 = \frac{\hbar}{m_e r_7}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.672) gives:

$$\frac{\hbar^2}{m_e r_7^3} = \frac{(Z-6)e^2}{4\pi\varepsilon_0 r_7^2} - \frac{3\hbar^2}{12m_e r_7^2 r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_7^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-7}{Z-6}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_7^4 m_e} 10\sqrt{\frac{3}{4}}$$
(13.673)

The quadratic equation corresponding to Eq. (13.673) is

$$r_{7}^{2} - \frac{\frac{\hbar^{2}}{m_{e}}}{\left(\frac{(Z-6)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{3}{12} - \frac{2}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)^{r_{7}} - \frac{\frac{\hbar^{2}}{m_{e}}\left[\frac{Z-7}{Z-6}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_{3}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-6)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{3}{12} - \frac{2}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} = 0$$
(13.674)

The solution of Eq. (13.674) using the quadratic formula is:

$$\frac{a_{0}}{\left((Z-6)-\left(\frac{3}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{\pm}} + \frac{20\sqrt{3}\left(\left[\frac{Z-7}{Z-6}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-6)-\left(\frac{3}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

$$r_{7} = \frac{20\sqrt{3}\left(\left[\frac{Z-7}{Z-6}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{2}$$

$$(13.675)$$

 $r_{r}$  in units of  $a_{0}$ 

The positive root of Eq. (13.675) must be taken in order that  $r_7 > 0$ . Substitution of

 $\frac{r_3}{a_0}$  = 0.59020 (Eq. (10.62) with Z = 8) into Eq. (13.675) gives

$$r_2 = 0.91088a_0 \tag{13.676}$$

15 ENERGIES OF THE 2p SHELL OF THE OXYGEN ATOMS OF THE

#### **OXYGEN MOLECULE**

The central forces on the 2p shell of each O are increased with the formation of the  $\sigma$  MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the two O atoms at the new radius are calculated and added to the energy of the  $\sigma$  MO to give the total energy of  $O_2$ . Then, the bond energy is determined from the total  $O_2$  energy.

The radius  $r_8$  of each oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 {(13.677)}$$

Using the initial radius  $r_8$  of each O atom and the final radius  $r_7$  of the O2p shell of  $O_2$  10 (Eq. (13.676)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(O_2, 2p)$  of the Coulombic energy change of the O2p electrons of both atoms is determined using Eq. (10.102):

$$E_{T}(O_{2}, 2p) = -2\sum_{n=4}^{6} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{7}} - \frac{1}{r_{8}}\right)$$

$$= -2(13.60580 \ eV)(0.09784)(2+3+4)$$

$$= -23.96074 \ eV$$
(13.678)

#### 15 FORCE BALANCE OF THE $\sigma$ MO OF THE OXYGEN MOLECULE

The force balance equation for the  $\sigma$ -MO of the oxygen molecule given by Eq. (11.200) and

Eqs. (13.633-13.634) with 
$$n_e = 2$$
 and  $|L| = \sqrt{\frac{3}{4}}\hbar$  is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi \varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(\frac{3}{2} + \frac{\sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$
 (13.679)

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D - \left(\frac{1}{2} + \frac{\sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$
 (13.680)

$$\left(\frac{5}{2} + \frac{\sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D$$
(13.681)

$$a = \left(\frac{5}{2} + \frac{\sqrt{\frac{3}{4}}}{Z}\right) a_0 \tag{13.682}$$

Substitution of Z = 8 into Eq. (13.682) gives

$$a = 2.60825a_0 = 1.38023 \ X \ 10^{-10} \ m \tag{13.683}$$

Substitution of Eq. (13.683) into Eq. (11.79) is

5 
$$c' = 1.14198a_0 = 6.04312 \times 10^{-11} m$$
 (13.684)

The internuclear distance given by multiplying Eq. (13.684) by two is

$$2c' = 2.28397a_0 = 1.20862 \ X \ 10^{-10} \ m \tag{13.685}$$

The experimental bond distance is [28]

$$2c' = 1.20752 \times 10^{-10} m \tag{13.686}$$

10 Substitution of Eqs. (13.683-13.684) into Eq. (11.80) is

$$b = c = 2.34496a_0 = 1.24090 \ X \ 10^{-10} \ m \tag{13.687}$$

Substitution of Eqs. (13.683-13.684) into Eq. (11.67) is

$$e = 0.43783 \tag{13.688}$$

Using the electron configuration of  $O_2$  (Eq. (13.667)), the radii of the  $O1s = 0.12739a_0$  (Eq.

15 (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = 0.91088a_0$  (Eq. (13.676)) shells and the parameters of the  $\sigma$  MO of  $O_2$  given by Eqs. (13.3-13.4), (13.683-13.685), and (13.687-13.688), the dimensional diagram and charge-density of the  $O_2$  MO are shown in Figures 21 and 22, respectively.

# 20 SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE OXYGEN MOLECULE

The energies of the  $O_2$   $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (13.683-13.684) and (13.687)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$ :

$$V_e = \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -22.37716 \, eV$$
 (13.689)

25 
$$V_{p} = \frac{e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} = 11.91418 \, eV \tag{13.690}$$

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$$T = \frac{\hbar^2}{2m_* a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 4.28968 \ eV$$
 (13.691)

$$V_{m} = \frac{-h^{2}}{4m_{*}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -2.14484 \ eV$$
 (13.692)

$$E_T = V_e + T + V_m + V_p (13.693)$$

Substitution of Eqs. (11.79) and (13.689-13.692) into Eq. (13.693) gives

$$E_{T}(O_{2},\sigma) = \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left( \left(2 - \frac{1}{2}\frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1 \right) = -8.31814 \, eV$$
 (13.694)

where  $E_T(O_2, \sigma)$  is the total energy of the  $\sigma$  MO of  $O_2$ . The sum,  $E_T(O_2)$ , of  $E_T(O_2, 2p)$ , the 2p AO contribution given by Eq. (13.678), and  $E_T(O_2, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.694) is:

$$E_{T}(O_{2}) = E_{T}(O_{2}, 2p) + E_{T}(O_{2}, \sigma)$$

$$= -23.96074 \ eV - 8.31814 \ eV$$

$$= -32.27888 \ eV$$
(13.695)

10

5

### VIBRATION OF O,

The vibrational energy levels of  $O_2$  may be solved by determining the Morse potential curve from the energy relationships for the transition from two O atoms whose parameters are given by Eqs. (10.154-10.163) to the two O atoms whose parameter  $r_7$  is given by Eq. (13.676) and the  $\sigma$  MO whose parameters are given by Eqs. (13.683-13.685) and (13.687-13.688). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

## THE DOPPLER ENERGY TERMS OF THE OXYGEN MOLECULE

The equations of the radiation reaction force of oxygen are the same as those of  $H_2$  with the substitution of the oxygen parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

5 
$$\omega = \sqrt{\frac{e^2}{4\pi\varepsilon_0 a^3}} = 9.81432 \, X \, 10^{16} \, rad/s$$
 (13.696)

where a is given by Eq. (13.683). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar \omega = \hbar 9.81432 \, X \, 10^{16} \, rad/s = 6.45996 \, eV$$
 (13.697)

In Eq. (11.181), substitution of  $E_T(O_2)$  for  $E_m$ , the mass of the electron,  $m_e$ , for M, and the 10 kinetic energy given by Eq. (13.697) for  $\overline{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\vec{E}_D \cong E_{h\nu} \sqrt{\frac{2\vec{E}_K}{Mc^2}} = -32.27888 \ eV \sqrt{\frac{2e(6.45996 \ eV)}{m_e c^2}} = -0.16231 \ eV$$
 (13.698)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $O_2$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (13.698) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental  $O_2$   $\omega_e$  of 1580.19  $cm^{-1}$  (0.19592 eV) [28] for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{osc}(O_2)$  is

$$\overline{E}_{osc}(O_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.699)

$$\overline{E}_{osc}(O_2) = -0.16231 \ eV + \frac{1}{2}(0.19592 \ eV) = -0.06435 \ eV$$
 (13.700)

### TOTAL AND BOND ENERGIES OF THE OXYGEN MOLECULE

 $E_{T+osc}(O_2)$ , the total energy of  $O_2$  including the Doppler term, is given by the sum of 25  $E_T(O_2)$  (Eq. (13.695)) and  $\bar{E}_{osc}(O_2)$  given by Eq. (13.700):

$$E_{T+osc}(O_{2}) = V_{e} + T + V_{m} + V_{p} + E_{T}(O_{2}, 2p) + \overline{E}_{osc}(O_{2})$$

$$= E_{T}(O_{2}, \sigma) + E_{T}(O_{2}, 2p) + \overline{E}_{osc}(O_{2})$$

$$= E_{T}(O_{2}) + \overline{E}_{osc}(O_{2})$$
(13.701)

$$E_{T+asc}(O_{2}) = \begin{cases} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left(2 - \frac{1}{2}\frac{a_{0}}{a}\right) \ln\frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1\right) - 2\sum_{n=4}^{6} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{7}} - \frac{1}{r_{8}}\right) \\ \left(1 + \sqrt{\frac{2\hbar\sqrt{\frac{e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{m_{e}}}\right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \\ = -32.27888 \ eV - 0.16231 \ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{cases}$$

$$(13.702)$$

From Eqs. (13.699-13.702), the total energy of the  $O_2$  MO is

$$E_{T+osc}(O_2) = -32.27888 \ eV + \overline{E}_{osc}(O_2)$$

$$= -32.27888 \ eV - 0.16231 \ eV + \frac{1}{2}(0.19592 \ eV)$$

$$= -32.34323 \ eV$$
(13.703)

5 where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

The  $O_2$  bond dissociation energy,  $E_D(O_2)$ , is given by the difference in the total energies of the two O atoms and  $E_{T+osc}(O_2)$ :

$$E_D(O_2) = 2E(O) - E_{T+asc}(O_2)$$
 (13.704)

where the energy of an oxygen atom is [6]

$$E(O) = -13.61806 \, eV \tag{13.705}$$

Thus, the  $O_2$  bond dissociation energy,  $E_D\left(O_2\right)$ , given by Eqs. (13.703-13.705) is

$$E_D(O_2) = -2(13.61806 \ eV) - E_{T+osc}(O_2)$$

$$= -27.23612 \ eV - (-32.34323 \ eV)$$

$$= 5.10711 \ eV$$
(13.706)

The experimental  $O_2$  bond dissociation energy from Ref. [46] and Ref. [47] is

$$E_D(O_2) = 5.11665 \ eV$$
 (13.707)

15 
$$E_D(O_2) = 5.116696 \ eV$$
 (13.708)

The results of the determination of bond parameters of  $O_2$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

5

#### **FLUORINE MOLECULE**

The fluorine molecule can be formed by the reaction of two fluorine atoms:

$$F + F \to F_2 \tag{13.709}$$

The bond in the fluorine molecule comprises a  $H_2$ -type molecular orbital (MO) with two paired electrons. The force balance equation and radius  $r_9$  of the 2p shell of F is derived in the Nine-Electron Atoms section. With the formation of the  $H_2$ -type MO by the contribution of a 2p electron from each F atom, a diamagnetic force arises between the remaining 2p electrons and the  $H_2$ -type MO. This force from each F causes the  $H_2$ -type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining 2p electrons of each F decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $F_2$  is  $1s_1^21s_2^22s_1^22s_2^22p_1^42p_2^4\sigma_{1,2}^2$  where the subscript designates the F atom, 1 or 2,  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

20

$$\begin{array}{c|cccc}
 & \sigma & \text{state} \\
\hline
 & \uparrow \downarrow \\
\hline
 & 1 \\
\hline
 & 0 \\
\hline
 & 1
\end{array}$$

$$\begin{array}{c|cccc}
 & \uparrow \downarrow \\
\hline
 & 0 \\
\hline
 & 1
\end{array}$$

$$\begin{array}{c|cccc}
 & \uparrow \downarrow \\
\hline
 & 1 \\
\hline
 &$$

Fluorine is predicted to be diamagnetic in agreement with observations [42].

# FORCE BALANCE OF THE $_{2p}$ SHELL OF THE FLUORINE ATOMS OF 5 THE FLUORINE MOLECULE

For each F atom, force balance for the outermost 2p electron of  $F_2$  (electron 8) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 8 and the other 2p-shell as well as the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Nine-Electron 10 Atoms section. The central Coulomb force on the outer-most 2p shell electron of  $F_2$  (electron 8) due to the nucleus and the inner seven electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z - 7)e^2}{4\pi\varepsilon_0 r_8^2} \mathbf{i}_{\mathbf{r}} \tag{13.711}$$

for  $r > r_7$ . The 2p shell possess an external electric field given by Eq. (10.92) for  $r > r_8$ .

15 The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the p-orbital contributions is the same as that of the reactant fluorine atoms given by Eq. (10.176) with  $r_8$  replacing  $r_9$ :

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right) \frac{\hbar^2}{4m_e r_{\rm g}^2 r_{\rm g}} \sqrt{s(s+1)} \mathbf{i}_{\rm r} = -\frac{2\hbar^2}{12m_e r_{\rm g}^2 r_{\rm g}} \sqrt{\frac{3}{4}} \mathbf{i}_{\rm r}$$
(13.712)

Thus,  $\mathbf{F}_{diamagnetic}$  due to the two filled 2p orbitals per F atom is twice that of  $N_2$  given by 20 Eq. (13.622) having one filled 2p orbital per N atom.  $\mathbf{F}_{mag}$  corresponding to the conserved spin and orbital angular momentum is also the same as that of the reactant fluorine atoms given by Eq. (10.177) and that of  $N_2$  given by Eq. (13.623) where the outer radius of the 2p shell of the F atoms of  $F_2$  is  $r_8$ .

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_8^2 r_3} \sqrt{s(s+1)} \mathbf{i_r}$$
 (13.713)

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_8$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is:

(13.718)

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-8}{Z-7}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_8^4} 10\sqrt{s(s+1)} \mathbf{i}_r$$
 (13.714)

In addition, the contribution of a 2p electron from each F atom in the formation of the  $\sigma$  MO gives rise to a paramagnetic force on the remaining paired 2p electrons. The force  $\mathbf{F}_{mag}$  3 is given by Eq. (13.625) wherein the radius is  $r_8$ :

5 
$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_g^3} \sqrt{s(s+1)} \mathbf{i}_r$$
 (13.715)

The radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.711)) and diamagnetic (Eqs. (13.712) and (13.714)), and paramagnetic (Eqs. (13.713) and (13.715)) forces as follows:

$$\frac{m_e v_8^2}{r_8} = \begin{pmatrix}
\frac{(Z-7)e^2}{4\pi\varepsilon_0 r_8^2} - \frac{2\hbar^2}{12m_e r_8^2 r_3} \sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_8^2 r_3} \sqrt{s(s+1)} \\
-\left[\frac{Z-8}{Z-7}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_5 \hbar^2}{r_8^4 m_e} 10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_8^3} \sqrt{s(s+1)}
\end{pmatrix}$$
(13.716)

10 Substitution of  $v_8 = \frac{\hbar}{m_e r_8}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.716) gives:

$$\frac{\hbar^{2}}{m_{e}r_{8}^{3}} - \frac{\hbar^{2}}{4m_{e}r_{8}^{3}} \sqrt{\frac{3}{4}} = \frac{(Z-7)e^{2}}{4\pi\varepsilon_{0}r_{8}^{2}} - \frac{2\hbar^{2}}{12m_{e}r_{8}^{2}r_{3}} \sqrt{\frac{3}{4}} + \frac{3\hbar^{2}}{Zm_{e}r_{8}^{2}r_{3}} \sqrt{\frac{3}{4}} - \left[\frac{Z-8}{Z-7}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_{3}\hbar^{2}}{r_{8}^{4}m_{e}} 10\sqrt{\frac{3}{4}}$$

$$(13.717)$$

The quadratic equation corresponding to Eq. (13.717) is

$$r_8^2 - \frac{\frac{\hbar^2}{m_e} \left( 1 - \frac{\sqrt{3}}{8} \right)}{\left( \frac{(Z - 7)e^2}{4\pi\varepsilon_0} - \left( \frac{2}{12} - \frac{3}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} r_8 - \frac{\frac{\hbar^2}{m_e} \left[ \frac{Z - 8}{Z - 7} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 10 \sqrt{\frac{3}{4}}}{\left( \frac{(Z - 7)e^2}{4\pi\varepsilon_0} - \left( \frac{2}{12} - \frac{3}{Z} \right) \frac{\hbar^2}{m_e r_3} \sqrt{\frac{3}{4}} \right)} = 0$$

The solution of Eq. (13.718) using the quadratic formula is:

15

$$a_{0}\left(1-\frac{\sqrt{3}}{8}\right) = \frac{1-\frac{\sqrt{3}}{8}}{\left((Z-7)-\left(\frac{2}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{2}} + \frac{20\sqrt{3}\left(\left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-7)-\left(\frac{2}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

$$r_{8} = \frac{241}{\left((Z-7)-\left(\frac{2}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

$$(13.719)$$

 $r_3$  in units of  $a_0$ 

The positive root of Eq. (13.719) must be taken in order that  $r_8 > 0$ . Substitution of  $\frac{r_3}{a_0} = 0.51382$  (Eq. (10.62) with Z = 9) into Eq. (13.719) gives

$$r_8 = 0.73318a_0 \tag{13.720}$$

ENERGIES OF THE  $_{2p}$  SHELL OF THE FLUORINE ATOMS OF THE FLUORINE MOLECULE

5

The central forces on the 2p shell of each F are increased with the formation of the  $\sigma$  MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the two F atoms at the new radius are calculated and added to the energy of the  $\sigma$  MO to give the total energy of  $F_2$ . Then, the bond energy is determined from the total  $F_2$  energy.

The radius  $r_9$  of each fluorine atom before bonding is given by Eq. (10.182):

$$r_9 = 0.78069a_0 \tag{13.721}$$

Using the initial radius  $r_9$  of each F atom and the final radius  $r_8$  of the F2p shell of  $F_2$  (Eq. (13.720)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(F_2, 2p)$  of the Coulombic energy change of the F2p electrons of both atoms is determined using Eq. (10.102):

$$E_T(F_2, 2p) = -2\sum_{n=4}^{7} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_8} - \frac{1}{r_9}\right)$$

$$= -2(13.60580 \ eV)(0.08301)(2+3+4+5)$$

$$= -31.62353 \ eV$$
(13.722)

## FORCE BALANCE OF THE $\sigma$ MO OF THE FLUORINE MOLECULE

The relativistic diamagnetic force  $\mathbf{F}_{diamagneticMO2}$  of  $F_2$  is one half that of  $N_2$  due to the two versus one filled 2p orbitals per atom at the focus. The force balance equation for the  $\sigma$ -5 MO of the fluorine molecule is given by Eq. (11.200) and Eqs. (13.633-13.634) with the correction of 1/2 due the two 2p orbitals per F after Eqs. (10.2-10.11),  $n_e = 2$ , and  $|L| = \hbar$ :

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi \varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(\frac{5}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.723}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D - \left(\frac{3}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.724}$$

$$\left(\frac{7}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D \tag{13.725}$$

10  $a = \left(\frac{7}{2} + \frac{1}{2Z}\right)a_0$  (13.726)

Substitution of Z = 9 into Eq. (13.726) gives

$$a = 3.55556a_0 = 1.88152 \ X \ 10^{-10} \ m \tag{13.727}$$

Substitution of Eq. (13.727) into Eq. (11.79) is

$$c' = 1.33333a_0 = 7.05569 \ X \ 10^{-11} \ m \tag{13.728}$$

15 The internuclear distance given by multiplying Eq. (13.728) by two is

$$2c' = 2.66667a_0 = 1.41114 \ X \ 10^{-10} \ m \tag{13.729}$$

The experimental bond distance is [28]

and 24, respectively.

$$2c' = 1.41193 \ X \ 10^{-10} \ m \tag{13.730}$$

Substitution of Eqs. (13.727-13.728) into Eq. (11.80) is

$$b = c = 3.29609a_0 = 1.74421 \times 10^{-10} m$$
 (13.731)

Substitution of Eqs. (13.727-13.728) into Eq. (11.67) is

$$e = 0.37500 \tag{13.732}$$

Using the electron configuration of  $F_2$  (Eq. (13.710)), the radii of the  $F1s = 0.11297a_0$  (Eq. (10.51)),  $F2s = 0.51382a_0$  (Eq. (10.62)), and  $F2p = 0.73318a_0$  (Eq. (13.720)) shells and the 25 parameters of the  $\sigma$  MO of  $F_2$  given by Eqs. (13.3-13.4), (13.727-13.728), and (13.731-13.732), the dimensional diagram and charge-density of the  $F_2$  MO are shown in Figures 23

## SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE FLUORINE MOLECULE

5 The energies of the  $F_2$   $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (13.683-13.684) and (13.687)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$ :

$$V_e = \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -16.09139 \ eV$$
 (13.733)

$$V_p = \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 10.20435 \, eV \tag{13.734}$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 2.26285 \ eV$$
 (13.735)

10  $V_m = \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -1.13143 \ eV$  (13.736)

$$E_T = V_e + T + V_m + V_p (13.737)$$

Substitution of Eqs. (11.79) and (13.733-13.736) into Eq. (13.737) gives

$$E_{T}(F_{2},\sigma) = \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left[ \left(2 - \frac{1}{2} \frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1\right] = -4.75562 \ eV$$
 (13.738)

where  $E_T(F_2, \sigma)$  is the total energy of the  $\sigma$  MO of  $F_2$ . The sum,  $E_T(F_2)$ , of  $E_T(F_2, 2p)$ ,

15 the 2p AO contribution given by Eq. (13.722), and  $E_T(F_2, \sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.738) is:

$$E_{T}(F_{2}) = E_{T}(F_{2}, 2p) + E_{T}(F_{2}, \sigma)$$

$$= -31.62353 \ eV - 4.75562 \ eV$$

$$= -36.37915 \ eV$$
(13.739)

### VIBRATION OF $F_2$

20 The vibrational energy levels of  $F_2$  may be solved by determining the Morse potential curve from the energy relationships for the transition from two F atoms whose parameters are given by Eqs. (10.174-10.183) to the two F atoms whose parameter  $r_8$  is given by Eq.

(13.720) and the σ MO whose parameters are given by Eqs. (13.727-13.729) and (13.731-13.732). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

### THE DOPPLER ENERGY TERMS OF THE FLUORINE MOLECULE

10 The equations of the radiation reaction force of fluorine are the same as those of  $H_2$  with the substitution of the fluorine parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{e^2}{4\pi\varepsilon_0 a^3}} = 6.16629 \, X \, 10^{15} \, rad/s \tag{13.740}$$

where a is given by Eq. (13.727). The kinetic energy,  $E_K$ , is given by Planck's equation 15 (Eq. (11.127)):

$$\widetilde{E}_K = \hbar \omega = \hbar 6.16629 \ X \ 10^{15} \ rad / s = 4.05876 \ eV$$
 (13.741)

In Eq. (11.181), substitution of  $E_T(F_2)$  for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.741) for  $\overline{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

20 
$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -36.37915 \ eV \sqrt{\frac{2e(4.05876 \ eV)}{m_e c^2}} = -0.14499 \ eV$$
 (13.742)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $F_2$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given 25 by Eq. (13.742) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental  $F_2$   $\omega_e$  of 916.64  $cm^{-1}$  (0.11365 eV) [28] for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{osc}(F_2)$  is

$$\overline{E}_{osc}(F_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.743)

$$\overline{E}_{asc}(F_2) = -0.14499 \ eV + \frac{1}{2}(0.11365 \ eV) = -0.08817 \ eV$$
 (13.744)

### TOTAL AND BOND ENERGIES OF THE FLUORINE MOLECULE

5  $E_{T+asc}(F_2)$ , the total energy of  $F_2$  including the Doppler term, is given by the sum of  $E_T(F_2)$  (Eq. (13.739)) and  $\overline{E}_{asc}(F_2)$  given by Eq. (13.744):

$$E_{T+asc}(F_{2}) = V_{e} + T + V_{m} + V_{p} + E_{T}(F_{2}, 2p) + \overline{E}_{asc}(F_{2})$$

$$= E_{T}(F_{2}, \sigma) + E_{T}(F_{2}, 2p) + \overline{E}_{asc}(F_{2})$$

$$= E_{T}(F_{2}) + \overline{E}_{asc}(F_{2})$$
(13.745)

$$E_{T+osc}(F_{2}) = \begin{cases} \left(\frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}}\left(\left(2 - \frac{1}{2}\frac{a_{0}}{a}\right)\ln\frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1\right) - 2\sum_{n=4}^{7}\frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}}\left(\frac{1}{r_{8}} - \frac{1}{r_{9}}\right)\right) \\ \left(\frac{2\hbar\sqrt{\frac{e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{m_{e}}\right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \\ = -36.37915 \ eV - 0.14499 \ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{cases}$$

$$(13.746)$$

From Eqs. (13.743-13.746), the total energy of the  $F_2$  MO is

$$E_{T+osc}(F_2) = -36.37915 \ eV + \overline{E}_{osc}(F_2)$$

$$= -36.37915 \ eV - 0.14499 \ eV + \frac{1}{2}(0.11365 \ eV)$$

$$= -36.46732 \ eV$$
(13.747)

where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

The  $F_2$  bond dissociation energy,  $E_D(F_2)$ , is given by the difference in the total energies of the two F atoms and  $E_{T+asc}(F_2)$ :

$$E_D(F_2) = 2E(F) - E_{T+osc}(F_2)$$
 (13.748)

15 where the energy of a fluorine atom is [6]

$$E(F) = -17.42282 \text{ eV} \tag{13.749}$$

Thus, the  $F_2$  bond dissociation energy,  $E_D(F_2)$ , given by Eqs. (13.747-13.749) is

$$E_D(F_2) = -2(17.42282 \, eV) - E_{T+osc}(F_2)$$

$$= -34.84564 \, eV - (-36.46732 \, eV)$$

$$= 1.62168 \, eV$$
(13.750)

The experimental  $F_2$  bond dissociation energy is [48]

5 
$$E_D(F_2) = 1.606 \, eV$$
 (13.751)

The results of the determination of bond parameters of  $F_2$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

10

#### **CHLORINE MOLECULE**

The chlorine molecule can be formed by the reaction of two chlorine atoms:

$$Cl + Cl \rightarrow Cl_2 \tag{13.752}$$

The chlorine molecule can be solved by using the hybridization approach used to solve the methane series  $CH_{n=1,2,3,4}$ . In the methane series, the 2s and 2p shells of carbon hybridize to form a single  $2sp^3$  shell to achieve an energy minimum, and in a likewise manner, the 3s and 3p shells of chlorine hybridize to form a single  $3sp^3$  shell which forms the bonding orbital of  $Cl_2$ .

#### 20 FORCE BALANCE OF Cl,

 $Cl_2$  has two spin-paired electrons in a chemical bond between the chlorine atoms. The  $Cl_2$  molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal  $H_2$  MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, each Cl atom could contribute a 3p electron to form a  $\sigma$  MO ( $H_2$ -type ellipsoidal MO) as in the case of  $N_2$ ,  $O_2$ , and  $F_2$ . However, such a bond is not possible with the outer Cl electrons in their ground state since the resulting 3p shells of chlorine atoms would overlap which is not energetically stable. Thus, when bonding, the chlorine 3s and 3p shells

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hybridize to form a single 3sp<sup>3</sup> shell to achieve an energy minimum.

The Cl electron configuration given in the Seventeen-Electron Atoms section is  $1s^2 2s^2 2p^6 3s^2 3p^5$ , and the orbital arrangement is

$$\begin{array}{cccc}
3p \text{ state} \\
\uparrow & \uparrow & \uparrow & \uparrow \\
\hline
1 & 0 & -1
\end{array}$$
(13.753)

5 corresponding to the ground state  ${}^{2}P_{3/2}^{0}$ . The radius  $r_{17}$  of the 3p shell given by Eq. (10.363) is

$$r_{17} = 1.05158a_0 \tag{13.754}$$

The energy of the chlorine 3p shell is the negative of the ionization energy of the chlorine atom given by Eq. (10.364). Experimentally, the energy is [6]

10 
$$E(3p \text{ shell}) = -E(\text{ionization}; Cl) = -12.96764 \text{ eV}$$
 (13.755)

The Cl3s atomic orbital (AO) combines with the Cl3p AOs to form a single  $3sp^3$  hybridized orbital (HO) with the orbital arrangement

where the quantum numbers  $(\ell, m_\ell)$  are below each electron. The total energy of the state is given by the sum over the seven electrons. Using only the largest-force terms of the outer most and next inner shell, the calculated energies for the chlorine atom and the ions: Cl,  $Cl^+$ ,  $Cl^{2+}$ ,  $Cl^{3+}$ ,  $Cl^{4+}$ ,  $Cl^{5+}$  and  $Cl^{6+}$  are given in Eqs. (10.363-10.364), (10.353-10.354), (10.331-10.332), (10.309-10.310), (10.288-10.289), (10.255-10.256), and (10.235-10.236), respectively. The sum  $E_T(Cl, 3sp^3)$  of the experimental energies of Cl and these ions is [6]

$$E_T(Cl,3sp^3) = \begin{pmatrix} 12.96764 \ eV + 23.814 \ eV + 39.61 \ eV + 53.4652 \ eV \\ +67.8 \ eV + 97.03 \ eV + 114.1958 \ eV \end{pmatrix}$$

$$= 408.88264 \ eV$$
(13.757)

The spin and orbital-angular-momentum interactions cancel such that the energy of the  $E_T(Cl,3sp^3)$  is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{3sp^3}$  of the  $Cl3sp^3$  shell may be calculated from the Coulombic energy using Eq. (10.102):

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$$r_{3sp^3} = \sum_{n=10}^{16} \frac{(Z-n)e^2}{8\pi\varepsilon_0 \left(e408.8826 \ eV\right)} = \frac{28e^2}{8\pi\varepsilon_0 \left(e408.8826 \ eV\right)} = 0.93172a_0 \tag{13.758}$$

where Z = 17. Using Eqs. (10.102) and (13.758), the Coulombic energy  $E_{Coulomb}(Cl, 3sp^3)$  of the outer electron of the  $Cl3sp^3$  shell is

$$E_{Coulomb}\left(Cl, 3sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{3sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.93172a_{0}} = -14.60295 \ eV \tag{13.759}$$

5 The calculated energy of the  $C2sp^3$  shell of 14.63489 eV given by Eq. (13.428), and nitrogen's calculated energy of 14.61664 eV given by Eq. (10.143) is a close match with  $E_{Coulomb}$  (Cl,  $3sp^3$ ).

The unpaired  $Cl3sp^3$  electron from each of two chlorine atoms combine to form a molecular orbital. The nuclei of the Cl atoms are along the internuclear axis and serve as the 10 foci. Due to symmetry, the other Cl electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the Cl MO involve only the two  $Cl3sp^3$  electrons. The forces are determined by these energies.

As in the case of  $H_2$ , the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $Cl3sp^3$  HO for distances shorter than the radius of the  $Cl3sp^3$  shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the nuclei and is continuous with the  $Cl3sp^3$  shell at each Cl atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $Cl3sp^3$  shell. As in the case with OH, NH, and CH (where the latter also demonstrates  $sp^3$  hybridization) the linear combination of the  $H_2$ -type ellipsoidal MO with each  $Cl3sp^3$  HO must involve a 25% contribution from the  $H_2$ -type ellipsoidal MO to the  $Cl3sp^3$  HO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $Cl_2$  MO must comprise two  $Cl3sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the two  $Cl3sp^3$  HOs:

$$2 Cl3sp^3 + 0.75 H_2 MO \rightarrow Cl_2 MO$$
 (13.760)

The force balance of the  $Cl_2$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.760) and the energy matching condition between the  $H_2$ -type-ellipsoidal-MO and  $Cl3sp^3$ -HO components of the MO.

As in the case with OH (Eq. (13.57)), NH (Eq. (13.247)), and CH (Eq. 13.429)), the  $H_2$ type ellipsoidal MO comprises 75% of the  $Cl_2$  MO; so, the electron charge density in Eq.
(11.65) is given by -0.75e. Since the chlorine atoms of  $Cl_2$  are hybridized and the kparameter is different from unity in order to meet the boundary constraints, both k and k'must comprise the corresponding hybridization factors. (In contrast, the chlorine atom of a C-Cl bond of an alkyl chloride is not hybridized, and only k' must comprise the
corresponding hybridization factor.) The force constant k' to determine the ellipsoidal
parameter c' in terms of the central force of the foci is given by Eq. (13.59), except that k' is
divided by two since the  $H_2$ -type-ellipsoidal-MO is physically divided between two  $Cl3sp^3$ HOs. In addition, the energy matching at both  $Cl3sp^3$  HOs further requires that k' be
corrected the hybridization factor given by Eq. (13.762). Thus, k' of the  $H_2$ -typeellipsoidal-MO component of the  $Cl_2$  MO is

$$k' = C_{C13sp^3HO} \frac{(0.75)}{2} \frac{2e^2}{4\pi\varepsilon_0} = 0.93172 \frac{(0.75)}{2} \frac{2e^2}{4\pi\varepsilon_0}$$
 (13.761)

The distance from the origin to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal Cl-Cl-bond b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the  $Cl_2$  MO. Since the  $Cl_2$ MO comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $Cl3sp^3$  HOs at each end of the molecule, the energy  $E(Cl,3sp^3)$  in Eq. (13.759) adds to that of the  $H_2$ -type ellipsoidal MO to give the total energy of the  $Cl_2$  MO. From the energy equation and the relationship between the axes, 25 the dimensions of the  $Cl_2$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ , T, and  $V_m$  are those of  $H_2$  (Eqs. (11.207-11.211)) except that they are corrected for electron hybridization. Hybridization gives rise to the  $Cl3sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(Cl,3sp^3)$  given by Eq. (13.759). To meet the

equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO with each  $Cl3sp^3$  HO, the electron energies are normalized by the ratio of  $14.60295\,eV$ , the magnitude of  $E_{Coulomb}\left(Cl,3sp^3\right)$  given by Eq. (13.759), and  $13.605804\,eV$ , the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). This normalizes the energies to match that of the Coulombic energy alone to meet the energy matching condition of the  $Cl_2$  MO under the influence of the two  $Cl3sp^3$  HOs bridged by the  $H_2$ -type-ellipsoidal MO. The hybridization energy factor  $C_{Cl3sp^3HO}$  is

$$C_{Cl3sp^3HO} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{3sp^3}}} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.93172 a_0}} = \frac{13.605804 \, eV}{14.60295 \, eV} = 0.93172$$
 (13.762)

The total energy  $E_T(Cl_2)$  of the  $Cl_2$  MO is given by the sum of the energies of the orbitals, 10 the  $H_2$ -type ellipsoidal MO and the two  $Cl3sp^3$  HOs, that form the hybridized  $Cl_2$  MO.  $E_T(Cl_2)$  follows from by Eq. (13.74) for OH, but the energy of the  $Cl3sp^3$  HO given by Eq. (13.759) is substituted for the energy of O and the  $H_2$ -type-ellipsoidal-MO energies are those of  $H_2$  (Eqs. (11.207-11.212)) multiplied by the electron hybridization factor rather than by the factor of 0.75:

$$E_{T}(Cl_{2}) = E_{T} + E_{Coulomb} (Cl, 3sp^{3})$$

$$= -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.93172) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.60295 \ eV$$
(13.763)

To match the boundary condition that the total energy of the entire the  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75),  $E_T(Cl_2)$  given by Eq. (13.763) is set equal to Eq. (13.75):

$$E_{T}(Cl_{2}) = -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.93172) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 14.60295 \ eV = -31.63537 \ eV$$
(13.764)

From the energy relationship given by Eq. (13.764) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $Cl_2$  MO can be solved.

Substitution of Eqs. (13.60) and (13.761) into Eq. (13.764) gives

20

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{4aa_0}{3(0.93172)}}} \left[ (0.93172)\left(2 - \frac{1}{2} \frac{a_0}{a}\right) \ln \frac{a + \sqrt{\frac{4aa_0}{3(0.93172)}}}{a - \sqrt{\frac{4aa_0}{3(0.93172)}}} - 1 \right] = e17.03242$$
(13.765)

The most convenient way to solve Eq. (13.765) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$5 a = 2.46500a_0 = 1.30442 X 10^{-10} m (13.766)$$

Substitution of Eq. (13.766) into Eq. (13.60) gives

$$c' = 1.87817a_0 = 9.93887 \ X \ 10^{-11} \ m \tag{13.767}$$

The internuclear distance given by multiplying Eq. (13.767) by two is

$$2c' = 3.75635a_0 = 1.98777 \times 10^{-10} m \tag{13.768}$$

10 The experimental bond distance is [28]

$$2c' = 1.988 X 10^{-10} m ag{13.769}$$

Substitution of Eqs. (13.766-13.767) into Eq. (13.62) gives

$$b = c = 1.59646a_0 = 8.44810 X 10^{-11} m ag{13.770}$$

Substitution of Eqs. (13.766-13.767) into Eq. (13.63) gives

$$15 e = 0.76194 (13.771)$$

The Cl nuclei comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $Cl3sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{3sp^3} = 0.93172a_0$  is the radius of the  $Cl3sp^3$  shell. Substitution of Eqs. (13.766-13.767)

20 into Eq. (13.261) gives

$$\theta' = 81.72^{\circ}$$
 (13.772)

Then, the angle  $\theta_{Cl3sp^3HO}$  the radial vector of the  $Cl3sp^3$  HO makes with the internuclear axis is

$$\theta_{Cl3sv^3HO} = 180^{\circ} - 81.72^{\circ} = 98.28^{\circ} \tag{13.773}$$

25 as shown in Figure 25. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$ 

between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $Cl3sp^3$  radial vector obeys the following relationship:

$$r_{3xp^3} \sin \theta_{Cl3sp^3HO} = 0.93172a_0 \sin \theta_{Cl3sp^3HO} = b \sin \theta_{H_2MO}$$
 (13.774)

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{0.93172a_0 \sin \theta_{Cl3sp^3HO}}{b} = \sin^{-1} \frac{0.93172a_0 \sin 98.28^{\circ}}{b}$$
(13.775)

with the use of Eq. (13.773). Substitution of Eq. (13.770) into Eq. (13.775) gives

$$\theta_{H,MO} = 35.28^{\circ}$$
 (13.776)

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$10 d_{H_0MO} = a\cos\theta_{H_0MO} (13.777)$$

Substitution of Eqs. (13.766) and (13.776) into Eq. (13.777) gives

$$d_{H,MO} = 2.01235a_0 = 1.06489 X 10^{-10} m ag{13.778}$$

The distance  $d_{Cl^3 \mathcal{P}^3 HO}$  along the internuclear axis from the origin of each Cl atom to the point of intersection of the orbitals is given by

$$d_{CI3,pp^3HO} = d_{H_2MO} - c' (13.779)$$

Substitution of Eqs. (13.768) and (13.778) into Eq. (13.779) gives

$$d_{Cl3sp^3HO} = 0.13417a_0 = 7.10022 X 10^{-12} m$$
 (13.780)

As shown in Eq. (13.760), a factor of 0.25 of the charge-density of the  $H_2$ -type ellipsoidal MO is distributed on each  $Cl3sp^3$  HO. Using the orbital composition of  $Cl_2$  (Eq. 20 (13.760)), the radii of the  $Cl1s = 0.05932a_0$  (Eq. (10.51)),  $Cl2s = 0.25344a_0$  (Eq. (10.62)),  $Cl2p = 0.31190a_0$  (Eq. (10.212)), and  $Cl3sp^3 = 0.93172a_0$  (Eq. (13.758)) shells, and the parameters of the  $Cl_2$  MO given by Eqs. (13.3-13.4), (13.766-13.768), and (13.770-13.771), the dimensional diagram and charge-density of the  $Cl_2$  MO comprising the linear combination of the  $H_2$ -type ellipsoidal MO and two  $Cl3sp^3$  HOs according to Eq. (13.760) 25 are shown in Figures 25 and 26, respectively.

#### ENERGIES OF Cl,

The energies of  $Cl_2$  are given by the substitution of the semiprincipal axes (Eqs. (13.766-13.767) and (13.770)) into the energy equations, (Eq. (13.763) and Eqs. (11.207-11.211) of  $H_2$ ) that are corrected for electron hybridization using Eq. (13.762):

$$V_e = (0.93172) \frac{-2e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -27.02007 \ eV$$
 (13.781)

$$V_p = \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 7.24416 \, eV \tag{13.782}$$

$$T = (0.93172) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 5.48074 \text{ eV}$$
 (13.783)

$$V_m = (0.93172) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -2.74037 \ eV$$
 (13.784)

$$10 \quad E_{T}(^{35}Cl_{2}) = -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.93172) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 14.60295 \ eV = -31.63849 \ eV$$

$$(13.785)$$

where  $E_T(Cl_2)$  is given by Eq. (13.763) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

#### 15 VIBRATION AND ROTATION OF Cl,

In  $Cl_2$ , the division of the  $H_2$ -type ellipsoidal MO between the two  $Cl3sp^3$  HOs and the hybridization must be considered in determining the vibrational parameters. One approach is to use Eq. (13.761) for the force constant and  $r_{3sp^3}$  given by Eq. (13.758) for the distance parameter of the central force in Eq. (11.213) since the  $H_2$ -type ellipsoidal MO is energy 20 matched to the  $Cl3sp^3$  HOs. With the substitution of the  $Cl_2$  parameters in Eqs. (11.213-11.217), the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{0.93172 \frac{(0.75)}{2} \frac{e^2}{8\pi\varepsilon_0 (r_{3sp^3})^3} \frac{e^2}{8\pi\varepsilon_0 (r_{3sp^3} + c')^3}}{\mu}}$$

$$= \sqrt{\frac{0.93172 \frac{(0.75)}{2} \frac{e^2}{8\pi\varepsilon_0 (0.93172)^3} \frac{e^2}{8\pi\varepsilon_0 (0.93172a_0 + 1.87817a_0)^3}}{\frac{35}{2} m_p}}$$

$$= 1.01438 \times 10^{14} \ rad/s$$
(13.786)

where c' is given by Eq. (13.767), and the reduced mass of  $^{35}Cl_2$  is given by:

$$\mu_{{}^{35}Cl_2} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(35)(35)}{35 + 35} m_p \tag{13.787}$$

where  $m_p$  is the proton mass. Thus, during bond formation, the perturbation of the orbit 5 determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency,  $\omega(0)$ , for  $^{35}Cl_2$  given by Eqs. (11.136), (11.148), and (13.786) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{301.19 \, Nm^{-1}}{\mu}} = 1.01438 \, X \, 10^{14} \, radians \, / \, s \tag{13.788}$$

where the reduced nuclear mass of  $^{35}Cl_2$  is given by Eq.(13.787) and the spring constant, k(0), given by Eqs. (11.136) and (13.786) is

$$k(0) = 301.19 \text{ Nm}^{-1}$$
 (13.789)

The  $^{35}Cl_2$  transition-state vibrational energy,  $E_{vib}(0)$  or  $\omega_e$ , given by Planck's equation (Eq. (11.127)) is:

$$E_{vib}(0) = \omega_e = \hbar\omega = \hbar 1.01438 X 10^{14} \ rad/s = 0.06677 \ eV = 538.52 \ cm^{-1}$$
 (13.790)

15  $\omega_e$ , from the experimental curve fit of the vibrational energies of  $^{35}Cl_2$  is [28]

$$\omega_e = 559.7 \text{ cm}^{-1} \tag{13.791}$$

Using Eqs. (13.112-13.118) with  $E_{vib}(0)$  given by Eq. (13.790) and  $D_0$  given by Eq. (13.807), the  $^{35}Cl_2$   $v=1 \rightarrow v=0$  vibrational energy,  $E_{vib}(1)$  is

$$E_{vib}(1) = 0.0659 \ eV$$
 (531.70 cm<sup>-1</sup>) (13.792)

20 The experimental vibrational energy of  $^{35}Cl_2$  using  $\omega_e$  and  $\omega_e x_e$  [28] according to K&P [15]

$$E_{vib}(1) = 0.0664 \ eV \qquad (535.55 \ cm^{-1})$$
 (13.793)

Using Eq. (13.113) with  $E_{vib}$  (1) given by Eq. (13.792) and  $D_0$  given by Eq. (13.807), the anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{35}Cl_2$  is

$$\omega_0 x_0 = 3.41 \text{ cm}^{-1} \tag{13.794}$$

5 The experimental anharmonic perturbation term,  $\omega_0 x_0$ , of  $^{35}Cl_2$  [28] is

$$\omega_0 x_0 = 2.68 \ cm^{-1} \tag{13.795}$$

The vibrational energies of successive states are given by Eqs. (13.790), (13.112), and (13.794).

Using Eqs. (13.133-13.134) and the internuclear distance, r = 2c', and reduced mass of  ${}^{35}Cl_2$  10 given by Eqs. (13.768) and (13.787), respectively, the corresponding  $B_e$  is

$$B_e = 0.2420 \text{ cm}^{-1} \tag{13.796}$$

The experimental  $B_e$  rotational parameter of  $^{35}Cl_2$  is [28]

$$B_e = 0.2440 \ cm^{-1} \tag{13.797}$$

#### 15 THE DOPPLER ENERGY TERMS OF Cl<sub>2</sub>

The equations of the radiation reaction force of the symmetrical  $Cl_2$  MO are the given by Eqs. (11.231-11.233) with the substitution of the  $Cl_2$  parameters and the substitution of the force factor of Eq. (13.761). The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.93172 \frac{(0.75)}{2} \frac{e^2}{4\pi \varepsilon_0 a^3}}{m_e}} = 6.31418 \times 10^{15} \ rad/s$$
 (13.798)

where a is given by Eq. (13.766). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar \omega = \hbar 1.6.31418 \, X \, 10^{15} \, rad \, / \, s = 4.15610 \, eV$$
 (13.799)

In Eq. (11.181), substitution of the total energy of  $Cl_2$ ,  $E_T(Cl_2)$ , (Eq. (13.764)) for  $E_{h\nu}$ , the 25 mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.799) for  $\overline{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit;

$$\overline{E}_{D} \cong E_{hv} \sqrt{\frac{2\overline{E}_{K}}{Mc^{2}}} = -31.63537 \ eV \sqrt{\frac{2e(4.15610 \ eV)}{m_{e}c^{2}}} = -0.12759 \ eV$$
 (13.800)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $Cl_2$  due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (13.800) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of  $Cl_2$ . Using the experimental  $^{35}Cl_2$   $\omega_e$  of 559.7 cm<sup>-1</sup> (0.06939 eV) [28] for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{osc}(^{35}Cl_2)$  is

$$\overline{E}_{osc}\left(^{35}Cl_{2}\right) = \overline{E}_{D} + \overline{E}_{Kvib} = \overline{E}_{D} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.801)

10 
$$\bar{E}_{osc}(^{35}Cl_2) = -0.12759 \ eV + \frac{1}{2}(0.06939 \ eV) = -0.09289 \ eV$$
 (13.802)

#### TOTAL AND BOND ENERGIES OF Cl,

 $E_{T+osc}(^{35}Cl_2)$ , the total energy of the  $^{35}Cl_2$  radical including the Doppler term, is given by the sum of  $E_T(Cl_2)$  (Eq. (13.764)) and  $\overline{E}_{osc}(^{35}Cl_2)$  given by Eq. (13.802):

$$E_{T+osc}\left({}^{35}Cl_{2}\right) = V_{e} + T + V_{m} + V_{p} + E_{Coulomb}\left(Cl, 3sp^{3}\right) + \overline{E}_{osc}\left({}^{35}Cl_{2}\right)$$

$$= E_{T}\left(Cl_{2}\right) + \overline{E}_{osc}\left({}^{35}Cl_{2}\right)$$
(13.803)

$$E_{T+osc}(^{35}Cl_{2}) = \begin{cases} \left(\frac{-e^{2}}{8\pi\varepsilon_{0}c'}\left[(0.93172)\left(2 - \frac{1}{2}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] - 14.60295 \ eV\right) \\ \left(\frac{2\hbar\sqrt{\frac{0.93172\frac{(0.75)}{2}\frac{e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}\right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{cases}$$

$$= -31.63537 \ eV - 0.12759 \ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

(13.804)

From Eqs. (13.801-13.804), the total energy of  $^{35}Cl_2$  is

$$E_{T+\alpha se} \left( {}^{35}Cl_2 \right) = -31.63537 \ eV + \overline{E}_{\alpha se} \left( {}^{35}Cl_2 \right)$$

$$= -31.63537 \ eV - 0.12759 \ eV + \frac{1}{2} (0.06939 \ eV)$$

$$= -31.72826 \ eV$$
(13.805)

where the experimental  $\omega_e$  (Eq. (13.791)) was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

The  $Cl_2$  bond dissociation energy,  $E_D(^{35}Cl_2)$ , is given by the difference between the total energies of the two  $Cl3sp^3$  HOs and  $E_{T+osc}(^{35}Cl_2)$ :

5 
$$E_D(^{35}Cl_2) = 2E_{Coulomb}(Cl, 3sp^3) - E_{T+osc}(^{35}Cl_2)$$
 (13.806)

 $E_{Coulomb}\left(Cl,3sp^3\right)$  is given by Eq. (13.759); thus, the  $^{35}Cl_2$  bond dissociation energy,  $E_D\left(^{35}Cl_2\right)$ , given by Eqs. (13.759) and (13.805-13.806) is

$$E_{D}(^{35}Cl_{2}) = -2(14.60295 \ eV) - E_{T+osc}(^{35}Cl_{2})$$

$$= -29.20590 \ eV - (-31.72826 \ eV)$$

$$= 2.52236 \ eV$$
(13.807)

The experimental  $^{35}Cl_2$  bond dissociation energy is [49]

$$E_D(^{35}Cl_2) = 2.51412 \ eV \tag{13.808}$$

The results of the determination of bond parameters of  $Cl_2$  are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

15

#### CARBON NITRIDE RADICAL

The carbon nitride radical can be formed by the reaction of carbon and nitrogen atoms:

$$C + N \to CN \tag{13.809}$$

The bond in carbon nitride radical comprises a  $H_2$ -type molecular orbital (MO) with two paired electrons. The force balance equations and radii,  $r_6$  and  $r_7$ , of the 2p shell of C and N are derived in the Six-Electron Atoms section and Seven-Electron Atoms section, respectively. With the formation of the  $H_2$ -type MO by the contribution of a 2p electron from each of the C and N atoms, a diamagnetic force arises between the remaining 2p electrons of each atom and the  $H_2$ -type MO. This force from each atom causes the  $H_2$ -type

MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining 2p electrons of each atom decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of CN is  $C1s^2N1s^2C2s^2N2s^2C2p^1N2p^2\sigma_{C,N}^2$  where  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

$$\begin{array}{ccc}
\sigma & \text{state} \\
 & \uparrow \downarrow \\
\hline
2p & \text{state} \\
 & \uparrow \downarrow \\
\hline
0 & 0
\end{array}$$
(13.810)

$$\begin{array}{cccc}
2s & \text{state} \\
 & \uparrow \downarrow \\
\hline
 & \uparrow \downarrow \\
\hline
 & C & N
\end{array}$$

10

The carbon nitride radical is predicted to be weakly paramagnetic.

# FORCE BALANCE OF THE $_{2p}$ SHELL OF THE CARBON ATOM OF THE CARBON NITRIDE RADICAL

- 15 For the C atom, force balance for the outermost 2p electron of CN (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 5 and the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Six-Electron Atoms section. The central Coulomb force on the outer-most 2p shell electron of CN (electron 5) due to the nucleus
- 20 and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_s^2} \mathbf{i}_{\mathbf{r}} \tag{13.811}$$

for  $r > r_4$ . The 2p shell possess an external electric field given by Eq. (10.92) for  $r > r_5$ .

The single unpaired carbon 2p electron gives rise to a diamagnetic force on the  $\sigma$ -MO as given by Eqs. (13.835-13.839). The corresponding Newtonian reaction force cancels  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82). The energy is minimized with conservation of angular momentum.

5 This condition is met when

$$\mathbf{F}_{diamagnetic} = 0 \tag{13.812}$$

And,  $F_{mag 2}$  corresponding to the maximum orbital angular momentum of the three 2p orbitals given by Eq. (10.89) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_5^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
 (13.813)

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_5$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is:

$$\mathbf{F}_{diamognetic\ 2} = -\left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_5^4} 10\sqrt{s(s+1)} \mathbf{i}_r$$
 (13.814)

The radius of the 2p shell is calculated by equating the outward centrifugal force to 15 the sum of the electric (Eq. (13.811)) and diamagnetic (Eqs. (13.812) and (13.814)), and paramagnetic (Eq. (13.813)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \begin{pmatrix} \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} + \frac{3\hbar^2}{Zm_e r_5^2 r_3} \sqrt{s(s+1)} \\ -\left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_5 \hbar^2}{r_5^4 m_e} 10\sqrt{s(s+1)} \end{pmatrix}$$
(13.815)

Substitution of  $v_5 = \frac{\hbar}{m_e r_5}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.815) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} + \frac{3\hbar^2}{Zm_e r_5^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_5 \hbar^2}{r_5^4 m_e} 10\sqrt{\frac{3}{4}}$$
(13.816)

20 The quadratic equation corresponding to Eq. (13.816) is

$$r_{5}^{2} - \frac{\frac{\hbar^{2}}{m_{e}}}{\left(\frac{(Z-4)e^{2}}{4\pi\varepsilon_{0}} + \frac{3\hbar^{2}}{Zm_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} r_{5} - \frac{\frac{\hbar^{2}}{m_{e}}\left[\frac{Z-5}{Z-4}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_{3}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-4)e^{2}}{4\pi\varepsilon_{0}} + \frac{3\hbar^{2}}{Zm_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} = 0$$

(13.817)

The solution of Eq. (13.817) using the quadratic formula is:

$$\frac{a_0}{\left((Z-4) + \frac{3\sqrt{3}}{Z2r_3}\right)^{\frac{1}{2}}} \pm a_0 \left(\frac{1}{\left((Z-4) + \frac{3\sqrt{3}}{Z2r_3}\right)^2} + \frac{20\sqrt{3}\left(\left[\frac{Z-5}{Z-4}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-4) + \frac{3\sqrt{3}}{Z2r_3}\right)}\right)$$

$$r_5 = \frac{2}{2} \left(\frac{1}{Z-4} + \frac{3\sqrt{3}}{Z2r_3}\right) + \frac{1}{Z2r_3} + \frac{1}{Z2r_3}$$

 $r_3$  in units of  $a_0$ 

The positive root of Eq. (13.818) must be taken in order that  $r_5 > 0$ . Substitution of

5  $\frac{r_3}{a_0}$  = 0.84317 (Eq. (10.62) with Z = 6) into Eq. (13.818) gives

$$r_5 = 0.88084a_0 \tag{13.819}$$

### FORCE BALANCE OF THE 2p SHELL OF THE NITROGEN ATOM OF THE CARBON NITRIDE RADICAL

10 For the N atom, force balance for the outermost 2p electron of CN (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other 2p-shell as well as the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most 2p shell electron of CN (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} \mathbf{i_r} \tag{13.820}$$

for  $r > r_5$ . The 2p shell possess an external electric field given by Eq. (10.92) for  $r > r_6$ .

The forces to determine the radius of the N2p shell of N in CN are the same as 20 those of N in  $N_2$  except that in CN there is a contribution from the Newtonian reaction force that arises from the single unpaired carbon 2p electron. The energy is minimized with

conservation of angular momentum. This condition is met when  $\mathbf{F}_{diamagnetic}$  of N in CN is canceled by the  $\sigma$ -MO -reaction force. Eq. (13.622) becomes

$$\mathbf{F}_{diamognetic} = 0 \tag{13.821}$$

And,  $F_{mag 2}$  corresponding to the conserved orbital angular momentum of the three orbitals 5 given by Eq. (10.89) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i_r}$$
 (13.822)

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_6$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is

10 
$$\mathbf{F}_{diamagnetic 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10\sqrt{s(s+1)} \mathbf{i_r}$$
 (13.823)

The N forces  $\mathbf{F}_{ele}$ ,  $\mathbf{F}_{mag~2}$ ,  $\mathbf{F}_{diamagnetic~2}$ , and  $\mathbf{F}_{mag~3}$  of CN are the same as those of  $N_2$  given by Eqs. (13.621) and (13.623-13.624), respectively. In both cases, the contribution of a 2p electron from the N atom in the formation of the  $\sigma$  MO gives rise to a paramagnetic force on the remaining two 2p electrons that pair. Thus, the force,  $\mathbf{F}_{mag~3}$  of CN, given by 15 Eq. (13.625) is

$$\mathbf{F}_{mag 3} = \frac{\hbar^2}{4m_r r_6^3} \sqrt{s(s+1)} \mathbf{i}_r \tag{13.824}$$

The radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.820)) and diamagnetic (Eqs. (13.821) and (13.823)), and paramagnetic (Eqs. (13.822) and (13.824)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left( \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} + \frac{3\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} - \left[ \frac{Z-6}{Z-5} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10 \sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \right)$$
(13.825)

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.626) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3} \sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} + \frac{3\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10\sqrt{\frac{3}{4}}$$
(13.826)

262 The quadratic equation corresponding to Eq. (13.826) is

$$r_{6}^{2} - \frac{\frac{\hbar^{2}}{m_{e}} \left(1 - \frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z - 5)e^{2}}{4\pi\varepsilon_{0}} + \frac{3\hbar^{2}}{Zm_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} r_{6} - \frac{\frac{\hbar^{2}}{m_{e}} \left[\frac{Z - 6}{Z - 5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) r_{3} 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z - 5)e^{2}}{4\pi\varepsilon_{0}} + \frac{3\hbar^{2}}{Zm_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} = 0$$
(13.827)

The solution of Eq. (13.827) using the quadratic formula is:

5

$$\frac{a_0 \left(1 - \frac{\sqrt{3}}{8}\right)}{\left((Z - 5) + \frac{3\sqrt{3}}{Z2r_3}\right)^{\pm} a_0} + \frac{\left(\frac{1 - \frac{\sqrt{3}}{8}}{(Z - 5) + \frac{3\sqrt{3}}{Z2r_3}}\right)^2}{2\left((Z - 5) + \frac{3\sqrt{3}}{Z2r_3}\right)}$$

$$r_6 = \frac{1 - \frac{\sqrt{3}}{8}}{\left((Z - 5) + \frac{3\sqrt{3}}{Z2r_3}\right)}$$

$$(13.828)$$

 $r_3$  in units of  $a_0$ 

The positive root of Eq. (13.828) must be taken in order that  $r_6 > 0$ . Substitution of

$$\frac{r_3}{a_0}$$
 = 0.69385 (Eq. (10.62) with Z = 7) into Eq. (13.828) gives

$$r_6 = 0.76366a_0 \tag{13.829}$$

### 10 ENERGIES OF THE 2p SHELLS OF THE CARBON AND NITROGEN ATOMS OF THE CARBON NITRIDE RADICAL

The central forces on the 2p shell of the C and N atoms are increased with the formation of the  $\sigma$  MO which reduces each shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the C and N atoms at the new radii are calculated and added to the energy of the  $\sigma$  MO to give the total energy of CN. Then, the bond energy is determined from the total CN energy.

The radius  $r_6$  of the carbon atom before bonding is given by Eq. (10.122):

$$r_6 = 1.20654a_0 \tag{13.830}$$

Using the initial radius  $r_6$  of the C atom and the final radius  $r_5$  of the C2p shell of CN (Eq.

(13.819)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(CN,C2p)$  of the Coulombic energy change of the C2p electron is determined using Eq. (10.102):

$$E_T(CN, C2p) = -\sum_{n=4}^4 \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_5} - \frac{1}{r_6}\right) = -(13.60580 \ eV)(0.30647)(2) = -8.33948 \ eV$$
(13.831)

The radius  $r_2$  of the nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084a_0 \tag{13.832}$$

Using the initial radius  $r_7$  of the N atom and the final radius  $r_6$  of the N2p shell of CN (Eq. (13.829)) and by considering that the central Coulombic field decreases by an integer for 10 each successive electron of the shell, the sum  $E_T(CN, N2p)$  of the Coulombic energy change of the N2p electron is determined using Eq. (10.102):

$$E_{T}(CN, N2p) = -\sum_{n=4}^{5} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{6}} - \frac{1}{r_{7}}\right)$$

$$= -(13.60580 \ eV)(0.23518)(2+3)$$

$$= -15.99929 \ eV$$
(13.833)

#### FORCE BALANCE OF THE $\sigma$ MO OF THE CARBON NITRIDE RADICAL

15 The diamagnetic force  $\mathbf{F}_{diamagnetic MO1}$  for the  $\sigma$ -MO of the CN molecule due to the two paired electrons in the N2p shell given by Eq. (13.633) with  $n_e = 2$  is:

$$\mathbf{F}_{diamognettcMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi} \tag{13.834}$$

The force  $\mathbf{F}_{diamagneticMO2}$  is given by Eq. (13.634) except that the force is the summed over the individual diamagnetic-force terms due to each component of angular momentum  $|L_i|$  acting on the electrons of the  $\sigma$ -MO from each atom having a nucleus of charge  $Z_j$  at one of the foci of the  $\sigma$ -MO:

$$\mathbf{F}_{diamagneticMO2} = \sum_{i,j} \frac{|L_i| \hbar}{Z_j 2m_e a^2 b^2} D\mathbf{i}_{\xi}$$
 (13.835)

Using Eqs. (11.200), (13.633-13.634), and (13.834-13.835), the force balance for the  $\sigma$ -MO of the carbon nitride radical comprising carbon with charge  $Z_1 = 6$  and  $|L_1| = \hbar$  and

 $\left|L_{2}\right| = \sqrt{\frac{3}{4}}\hbar$  and nitrogen with  $Z_{2} = 7$  and  $\left|L_{3}\right| = \hbar$  is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$
(13.836)

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D - \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$
 (13.837)

$$\left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D$$
(13.838)

5  $a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) a_0$  (13.839)

Substitution of  $Z_1 = 6$  and  $Z_2 = 7$  into Eq. (13.839) gives

$$a = 2.45386a_0 = 1.29853 \ X \ 10^{-10} \ m \tag{13.840}$$

Substitution of Eq. (13.840) into Eq. (11.79) is

$$c' = 1.10767a_0 = 5.86153 \ X \ 10^{-11} \ m \tag{13.841}$$

10 The internuclear distance given by multiplying Eq. (13.841) by two is

$$2c' = 2.21534a_0 = 1.17231 \times 10^{-10} m$$
 (13.842)

The experimental bond distance from Ref. [28] is

$$2c' = 1.17181 \ X \ 10^{-10} \ m \tag{13.843}$$

Substitution of Eqs. (13.840-13.841) into Eq. (11.80) is

15 
$$b = c = 2.18964a_0 = 1.15871 \times 10^{-10} m$$
 (13.844)

Substitution of Eqs. (13.840-13.841) into Eq. (11.67) is

$$e = 0.45140 \tag{13.845}$$

Using the electron configuration of CN (Eq. (13.810), the radii of the  $C1s = 0.17113a_0$  (Eq. (10.51)),  $C2s = 0.84317a_0$  (Eq. (10.62)),  $C2p = 0.88084a_0$  (Eq. (13.819)),  $N1s = 0.14605a_0$  20 (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)), and  $N2p = 0.76366a_0$  (Eq. (13.829)) shells

265

and the parameters of the  $\sigma$  MO of CN given by Eqs. (13.3-13.4), (13.840-13.842), and (13.844-13.845), the dimensional diagram and charge-density of the CN MO are shown in Figures 27 and 28, respectively.

### 5 SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE CARBON NITRIDE RADICAL

The energies of the CN  $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (13.840-13.841) and (13.844)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$ :

$$V_e = \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -23.90105 \ eV$$
 (13.846)

10 
$$V_p = \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 12.28328 \ eV \tag{13.847}$$

$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 4.87009 \ eV$$
 (13.848)

$$V_{m} = \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -2.43504 \ eV$$
 (13.849)

$$E_T = V_e + T + V_m + V_p ag{13.850}$$

Substitution of Eqs. (11.79) and (13.846-13.849) into Eq. (13.850) gives

15 
$$E_{T}(CN,\sigma) = \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left[ \left(2 - \frac{1}{2} \frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 1\right] = -9.18273 \ eV$$
 (13.851)

where  $E_T(CN,\sigma)$  is the total energy of the  $\sigma$  MO of CN. The sum,  $E_T(CN)$ , of  $E_T(CN,C2p)$ , the C2p AO contribution given by Eq. (13.831),  $E_T(CN,N2p)$ , the N2p AO contribution given by Eq. (13.833), and  $E_T(CN,\sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.851) is:

$$E_{T}(CN) = E_{T}(CN, C2p) + E_{T}(CN, N2p) + E_{T}(N_{2}, \sigma)$$

$$= -8.33948 \ eV - 15.99929 \ eV - 9.18273 \ eV$$

$$= -33.52149 \ eV$$
(13.852)

#### VIBRATION OF CN

The vibrational energy levels of CN may be solved by determining the Morse potential curve from the energy relationships for the transition from a C atom and N atom whose parameters are given by Eqs. (10.115-10.123) and (10.134-10.143), respectively, to a C atom 5 whose parameter  $r_5$  is given by Eq. (10.819), a N atom whose parameter  $r_6$  is given by Eq. (13.829), and the  $\sigma$  MO whose parameters are given by Eqs. (13.840-13.842) and (13.844-13.845). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter 10 (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

#### THE DOPPLER ENERGY TERMS OF THE CARBON NITRIDE RADICAL

15 The equations of the radiation reaction force of CN are the same as those of  $H_2$  with the substitution of the CN parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{e^2}{4\pi\varepsilon_0 a^3}} = 1.07550 \, X \, 10^{16} \, rad/s \tag{13.853}$$

where a is given by Eq. (13.840). The kinetic energy,  $E_K$ , is given by Planck's equation 20 (Eq. (11.127)):

$$\overline{E}_K = \hbar \omega = \hbar 1.07550 \, X \, 10^{16} \, rad \, / \, s = 7.07912 \, eV$$
 (13.854)

In Eq. (11.181), substitution of  $E_T(CN)$  for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.854) for  $\overline{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

25 
$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -33.59603 \ eV \sqrt{\frac{2e(7.07912 \ eV)}{m_e c^2}} = -0.17684 \ eV$$
 (13.855)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the CN MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation

of the electrons and nuclei,  $\overline{E}_{ose}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (13.855) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental CN  $\omega_e$  of 2068.59  $cm^{-1}$  (0.25647 eV) [28] for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{ose}(CN)$  is

$$\overline{E}_{osc}(CN) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.856)

$$\overline{E}_{osc}(CN) = -0.17684 \ eV + \frac{1}{2}(0.25647 \ eV) = -0.04860 \ eV$$
 (13.857)

#### TOTAL AND BOND ENERGIES OF THE CARBON NITRIDE RADICAL

 $E_{T+osc}(CN)$ , the total energy of CN including the Doppler term, is given by the sum of  $E_{T}(CN)$  (Eq. (13.852)) and  $\overline{E}_{osc}(CN)$  given by Eq. (13.857):

$$E_{T+osc}(CN) = V_e + T + V_m + V_p + E_T(CN, C2p) + E_T(CN, N2p) + \overline{E}_{asc}(CN)$$

$$= E_T(CN, \sigma) + E_T(CN, C2p) + E_T(CN, N2p) + \overline{E}_{osc}(CN)$$

$$= E_T(CN) + \overline{E}_{osc}(CN)$$
(13.858)

$$E_{T+osc}(CN) = \begin{cases} \frac{-e^2}{8\pi\varepsilon_0 \sqrt{\frac{aa_0}{2}}} \left(2 - \frac{1}{2} \frac{a_0}{a}\right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}}\right) \\ -\sum_{C,n=4}^{4} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_s} - \frac{1}{r_6}\right) - \sum_{N,n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_6} - \frac{1}{r_7}\right) \\ \left(1 + \sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\varepsilon_e a^3}}}{m_e c^2}}\right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{cases}$$

$$= -33.52149 \ eV - 0.17684 \ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

$$(13.859)$$

From Eqs. (13.856-13.859), the total energy of the CN MO is

$$E_{T+osx}(CN) = -33.52149 \, eV + \overline{E}_{osc}(CN)$$

$$= -33.52149 \, eV - 0.17684 \, eV + \frac{1}{2}(0.25647 \, eV)$$

$$= -33.56970 \, eV$$
(13.860)

where the experimental  $\omega_e$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The CN bond dissociation energy,  $E_D(CN)$ , is given by the difference between the sum of the energies of the C and N atoms and  $E_{T+osc}(CN)$ :

$$E_D(CN) = E(C) + E(N) - E_{T+osc}(CN)$$
(13.861)

5 where the energy of a carbon atom is [6]

$$E(C) = -11.26030 \ eV \tag{13.862}$$

and the energy of a nitrogen atom is [6]

10

Carrier Contract

$$E(N) = -14.53414 \ eV \tag{13.863}$$

Thus, the CN bond dissociation energy,  $E_D(CN)$ , given by Eqs. (13.860-13.863) is

$$E_D(CN) = -(11.26030 \ eV + 14.53414 \ eV) - E_{T+osc}(CN)$$

$$= -25.79444 \ eV - (-33.56970 \ eV)$$

$$= 7.77526 \ eV$$
(13.864)

The experimental CN bond dissociation energy is [50]

$$E_{D298}(CN) = 7.7731 \ eV$$
 (13.865)

The results of the determination of bond parameters of *CN* are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

#### CARBON MONOXIDE MOLECULE

The carbon monoxide molecule can be formed by the reaction of carbon and oxygen atoms:

$$20 C + O \rightarrow CO (13.866)$$

The bond in the carbon monoxide molecule comprises a double bond, a  $H_2$ -type molecular orbital (MO) with four paired electrons. The force balance equation and radius  $r_6$  of the 2p shell of C is derived in the Six-Electron Atoms section. The force balance equation and radius  $r_8$  of the 2p shell of C is derived in the Eight-Electron Atoms section. With the formation of the C and C atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the C electrons of C and the C electrons of C and the C and the C electrons of C electro

and O causes the  $H_2$ -type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining O2p electrons decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of CO is  $C1s^2O1s^2C2s^2O2s^2O2p^2\sigma_{C,O}^4$  where  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

$$\begin{array}{c|c}
\sigma \text{ state} \\
\uparrow \downarrow \uparrow \downarrow \\
\hline
2p \text{ state} \\
\hline
\downarrow 0 \\
\hline
2s \text{ state} \\
\hline
\uparrow \downarrow \qquad \uparrow \downarrow \\
\hline
C \qquad O
\end{array}$$
(13.867)

Carbon monoxide is predicted to be diamagnetic in agreement with observations [42].

FORCE BALANCE OF THE  $_{2p}$  SHELL OF THE OXYGEN ATOM OF THE CARBON MONOXIDE MOLECULE

For the O atom, force balance for the outermost 2p electron of CO (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other 2p electron as well as the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most 2p shell electron of CO (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} \mathbf{i}_{\mathbf{r}} \tag{13.868}$$

for  $r > r_5$ . The 2p shell possess a +2 external electric field given by Eq. (10.92) for  $r > r_6$ . The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the p-orbital contribution is given by:

5 
$$\mathbf{F}_{diamognetic} = -\left(\frac{1}{3}\right) \frac{\hbar^2}{4m_r r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r$$
 (13.869)

And,  $\mathbf{F}_{mag~2}$  corresponding to the conserved spin and orbital angular momentum given by Eq. (10.157) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{2\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i_r}$$
 (13.870)

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_6$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10\sqrt{s(s+1)} \mathbf{i}_r$$
 (13.871)

In addition, the contribution of two 2p electrons in the formation of the  $\sigma$  molecular orbital (MO) gives rise to a paramagnetic force on the remaining paired 2p electrons. The force  $\mathbf{F}_{mag 3}$  is given by Eq. (13.625) wherein the radius is  $r_6$ :

$$\mathbf{F}_{mog \ 3} = \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}}$$
 (13.872)

The radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.868)) and diamagnetic (Eqs. (13.869) and (13.871)), and paramagnetic (Eqs. (13.870) and (13.872)) forces as follows:

$$\frac{m_{e}v_{6}^{2}}{r_{6}} = \frac{\left(\frac{(Z-5)e^{2}}{4\pi\varepsilon_{0}r_{6}^{2}} - \frac{\hbar^{2}}{12m_{e}r_{6}^{2}r_{3}}\sqrt{s(s+1)} + \frac{2\hbar^{2}}{Zm_{e}r_{6}^{2}r_{3}}\sqrt{s(s+1)}\right)}{-\left[\frac{Z-6}{Z-5}\right]\left(1 - \frac{\sqrt{2}}{2}\right)\frac{r_{3}\hbar^{2}}{r_{6}^{4}m_{e}}10\sqrt{s(s+1)} + \frac{\hbar^{2}}{4m_{e}r_{6}^{3}}\sqrt{s(s+1)}\right)}$$
(13.873)

Substitution of  $v_6 = \frac{\hbar}{m_0 r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.873) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3} \sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10\sqrt{\frac{3}{4}}$$

(13.874)

The quadratic equation corresponding to Eq. (13.874) is

$$r_{6}^{2} - \frac{\frac{\hbar^{2}}{m_{e}} \left(1 - \frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z - 5)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{1}{12} - \frac{2}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} r_{6} - \frac{\frac{\hbar^{2}}{m_{e}} \left[\frac{Z - 6}{Z - 5}\right] \left(1 - \frac{\sqrt{2}}{2}\right)r_{3}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z - 5)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{1}{12} - \frac{2}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} = 0$$
(13.875)

The solution of Eq. (13.875) using the quadratic formula is:

$$\frac{a_0 \left(1 - \frac{\sqrt{3}}{8}\right)}{\left((Z - 5) - \left(\frac{1}{12} - \frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)^{\pm} a_0} + \frac{\left((Z - 5) - \left(\frac{1}{12} - \frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)^2}{\left((Z - 5) - \left(\frac{1}{12} - \frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} + \frac{20\sqrt{3}\left(\left[\frac{Z - 6}{Z - 5}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z - 5) - \left(\frac{1}{12} - \frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}$$

$$r_6 = \frac{2}{2}$$
(13.876)

 $r_3$  in units of  $a_0$ 

The positive root of Eq. (13.876) must be taken in order that  $r_6 > 0$ . Substitution of

$$\frac{r_3}{a_0}$$
 = 0.59020 (Eq. (10.62) with Z = 8) into Eq. (13.876) gives

$$r_6 = 0.68835a_0 \tag{13.877}$$

# 10 ENERGIES OF THE 2s AND 2p SHELLS OF THE CARBON ATOM AND THE 2p SHELL OF THE OXYGEN ATOM OF THE CARBON MONOXIDE MOLECULE

With the formation of the  $H_2$ -type MO by the contribution of two 2p electrons from the C atom, the remaining outer-shell atomic electrons comprise the 2s electrons, which are unchanged by bonding with oxygen. However, the total energy of the CO molecule, which is subtracted from the sum of the energies of the carbon and oxygen atoms to determine the bond energy, is increased by the ionization energies of  $C^+$  and  $O^+$  given by Eqs. (10.113-10.114) and (10.152-10.153), respectively. Experimentally, the energies are [6]

$$E(ionization; C^+) = 24.38332 \, eV$$
 (13.878)

$$E(ionization; O^{+}) = 35.11730 \, eV$$
 (13.879)

In addition, the central forces on the 2p shell of the O atom are increased with the formation of the  $\sigma$  MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the O atom at the new radius are calculated and added to the ionization energies of  $C^+$  and  $O^+$ , and the energy of the  $\sigma$  MO to give the total energy of CO. Then, the bond energy is determined from the total CO energy.

The radius  $r_8$  of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 {(13.880)}$$

Using the initial radius  $r_8$  of the O atom and the final radius  $r_6$  of the O2p shell (Eq. 10 (13.877)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(O,2p)$  of the Coulombic energy change of the O2p electrons of the O atom is determined using Eq. (10.102):

$$E_T(O,2p) = -\sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_6} - \frac{1}{r_8}\right)$$

$$= -(13.60580 \ eV)(0.45275)(3+4)$$

$$= -43.11996 \ eV$$
(13.881)

### 15 FORCE BALANCE OF THE $\sigma$ MO OF THE CARBON MONOXIDE MOLECULE

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having +2e at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having +e at each focus. The diamagnetic force  $\mathbf{F}_{diamagneticMO1}$  for 20 the  $\sigma$ -MO of the CO molecule due to the two paired electrons in each of the C2s and O2p shells is given by Eq. (13.633) with  $n_e = 2$ :

$$\mathbf{F}_{diamogneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$
 (13.882)

The force  $\mathbf{F}_{diamagneticMO2}$  is given by Eqs. (13.634) and (13.835) as the sum of the contributions due to carbon with  $Z = Z_1$  and oxygen with  $Z = Z_2$ .  $\mathbf{F}_{diamagneticMO1}$  for CO with  $|L_i| = \hbar$  is

25 
$$\mathbf{F}_{diamogneticMO2} = \left(\frac{1}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$
 (13.883)

The force balance equation for the  $\sigma$ -MO of the carbon monoxide molecule given by Eqs. (11.200), (13.633-13.634), and (13.882-13.883) is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi \varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \left(\frac{1}{Z_1} + \frac{1}{Z_2}\right)\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$
(13.884)

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi \varepsilon_0 a b^2} D - \left(\frac{1}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$
 (13.885)

5 
$$\left(2 + \frac{1}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D$$
 (13.886)

$$a = \left(2 + \frac{1}{Z_1} + \frac{1}{Z_2}\right) a_0 \tag{13.887}$$

Substitution of  $Z_1 = 6$  and  $Z_2 = 8$  into Eq. (13.887) gives

$$a = 2.29167a_0 = 1.21270 X 10^{-10} m ag{13.888}$$

Substitution of Eq. (13.888) into Eq. (11.79) is

$$c' = 1.07044a_0 = 5.66450 X 10^{-11} m ag{13.889}$$

The internuclear distance given by multiplying Eq. (13.889) by two is

$$2c' = 2.14087a_0 = 1.13290 \ X \ 10^{-10} \ m \tag{13.890}$$

The experimental bond distance is [28]

$$2c' = 1.12823 \ X \ 10^{-10} \ m \tag{13.891}$$

15 Substitution of Eqs. (13.888-13.889) into Eq. (11.80) is

$$b = c = 2.02630a_0 = 1.07227 X 10^{-10} m ag{13.892}$$

Substitution of Eqs. (13.888-13.889) into Eq. (11.67) is

$$e = 0.46710 \tag{13.893}$$

Using the electron configuration of CO (Eq. (13.867)), the radii of the  $C1s = 0.17113a_0$  (Eq. (10.51)),  $C2s = 0.84317a_0$  (Eq. (10.62)),  $O1s = 0.12739a_0$  (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = 0.68835a_0$  (Eq. (13.877)) shells and the parameters of the  $\sigma$  MO of CO given by Eqs. (13.3-13.4), (13.888-13.890), and (13.892-13.893), the dimensional diagram and charge-density of the CO MO are shown in Figures 29 and 30, respectively.

### SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE CARBON MONOXIDE MOLECULE

The energies of the CO  $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. 5 (13.888-13.889) and (13.892)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$  except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the  $\sigma$ -MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -102.97635 \ eV$$
 (13.894)

$$V_p = 2^2 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 50.84210 \, eV \tag{13.895}$$

10 
$$T = 2\frac{\hbar^2}{2m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 11.23379 \ eV$$
 (13.896)

$$V_m = 2^2 \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -11.23379 \ eV$$
 (13.897)

$$E_T = V_e + T + V_m + V_p ag{13.898}$$

Substitution of Eqs. (11.79) and (13.894-13.897) into Eq. (13.898) gives

$$E_{T}(CO,\sigma) = \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left( 8\ln\frac{a+\sqrt{\frac{aa_{0}}{2}}}{a-\sqrt{\frac{aa_{0}}{2}}} - 4 \right) = -52.13425 \ eV$$
 (13.899)

15 where  $E_T(CO,\sigma)$  is the total energy of the  $\sigma$  MO of CO. The total energy of CO,  $E_T(CO)$ , is given by the sum of  $E(ionization; C^+)$ , the energy of the second electron of carbon (Eq. (13.878)) donated to the double bond,  $E(ionization; O^+)$ , the energy of the second electron of oxygen (Eq. (13.879)) donated to the double bond,  $E_T(O,2p)$ , the O2p AO contribution due to the decrease in radius with bond formation (Eq. (13.881)), and  $E_T(CO,\sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.899):

$$E_{T}(CO) = E(ionization; C^{+}) + E(ionization; O^{+}) + E_{T}(O, 2p) + E_{T}(CO, \sigma)$$

$$= 24.38332 \ eV + 35.11730 \ eV - 43.11996 \ eV - 52.13425 \ eV$$

$$= -35.75359 \ eV$$
(13.900)

#### VIBRATION OF CO

The vibrational energy levels of CO may be solved by determining the Morse potential curve from the energy relationships for the transition from a C atom and O atom whose parameters are given by Eqs. (10.115-10.123) and (10.154-10.163), respectively, to a C atom whose parameter r<sub>4</sub> is given by Eq. (10.61), an O atom whose parameter r<sub>6</sub> is given by Eq. (13.877), and the σ MO whose parameters are given by Eqs. (13.888-13.890) and (13.892-13.893). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

### THE DOPPLER ENERGY TERMS OF THE CARBON MONOXIDE 15 MOLECULE

The equations of the radiation reaction force of carbon monoxide are the same as those of  $H_2$  with the substitution of the CO parameters except that there is a factor of four increase in the central force in Eq. (11.231) due to the double bond. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{4e^2}{4\pi\varepsilon_0 a^3}} = 2.38335 \, X \, 10^{16} \, rad/s \tag{13.901}$$

where a is given by Eq. (13.888). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.38335 \, X \, 10^{16} \, rad \, / \, s = 15.68762 \, eV$$
 (13.902)

In Eq. (11.181), substitution of  $E_T(CO)$  for  $E_h$ , the mass of the electron,  $m_e$ , for M, and 25 the kinetic energy given by Eq. (13.902) for  $\overline{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_{D} \cong E_{h\nu} \sqrt{\frac{2\overline{E}_{K}}{Mc^{2}}} = -35.75359 \ eV \sqrt{\frac{2e(15.68762 \ eV)}{m_{e}c^{2}}} = -0.28016 \ eV \tag{13.903}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the CO MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{asc}$ , is given by the sum of the corresponding energies,  $\overline{E}_{D}$  given by Eq. (13.903) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental CO  $\omega_{e}$  of 2169.81  $cm^{-1}$  (0.26902 eV) [28] for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{osc}^{+}(CO)$  per bond is

$$\overline{E}'_{asc}(CO) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.904)

$$\overline{E}'_{osc}(CO) = -0.28016 \ eV + \frac{1}{2}(0.26902 \ eV) = -0.14564 \ eV \tag{13.905}$$

10 Since the  $\sigma$  MO bond is a double bond with twice a many electrons as a single bond,  $\overline{E}'_{osc}(CO)$  is multiplied by two to give

$$\overline{E}_{or}(CO) = -0.29129 \, eV \tag{13.906}$$

TOTAL AND BOND ENERGIES OF THE CARBON MONOXIDE

15 MOLECULE

 $E_{T+asc}(CO)$ , the total energy of CO including the Doppler term, is given by the sum of  $E_T(CO)$  (Eq. (13.900)) and  $\overline{E}_{osc}(CO)$  given by Eq. (13.906):

$$E_{T+osc}(CO) = \begin{pmatrix} V_e + T + V_m + V_p + E(ionization; C^+) \\ + E(ionization; O^+) + E_T(O, 2p) + \overline{E}_{osc}(CO) \end{pmatrix}$$

$$= \begin{pmatrix} E_T(CO, \sigma) + E(ionization; C^+) + E(ionization; O^+) \\ + E_T(O, 2p) + \overline{E}_{osc}(CO) \end{pmatrix}$$

$$= E_T(CO) + \overline{E}_{osc}(CO)$$
(13.907)

$$E_{T+ose}(CO) = \begin{cases} \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}} - 4\right) + E(ionization; C^+) \\ + E(ionization; O^+) - \sum_{o,n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_6} - \frac{1}{r_8}\right) \end{cases}$$

$$= -35.75359 \ eV - 2(0.28016 \ eV) + 2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$(13.908)$$

From Eqs. (13.906-13.908), the total energy of the CO MO is

$$E_{T+osc}(CO) = -35.75359 \ eV + \overline{E}_{osc}(CO)$$

$$= -35.75359 \ eV + (-0.29129 \ eV)$$

$$= -36.04488 \ eV$$
(13.909)

where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

The CO bond dissociation energy,  $E_D(CO)$ , is given by the difference between the sum of the energies of the C and O atoms and  $E_{T+osc}(CO)$ :

$$E_D(CO) = E(C) + E(O) - E_{T+osc}(CO)$$
(13.910)

where the energy of a carbon atom is [6]

$$E(C) = -11.26030 \ eV \tag{13.911}$$

10 and the energy of an oxygen atom is [6]

$$E(O) = -13.61806 \ eV \tag{13.912}$$

Thus, the CO bond dissociation energy,  $E_D(CO)$ , given by Eqs. (13.909-13.912) is

$$E_D(CO) = -(11.26030 \, eV + 13.61806 \, eV) - E_{T+asc}(CO)$$

$$= -24.87836 \, eV - (-36.04488 \, eV)$$

$$= 11.16652 \, eV$$
(13.913)

The experimental CO bond dissociation energy is [49]

15 
$$E_{D298}(CO) = 11.15696 \, eV$$
 (13.914)

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The results of the determination of bond parameters of CO are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

5

#### NITRIC OXIDE RADICAL

The nitric oxide radical can be formed by the reaction of nitrogen and oxygen atoms:

 $N + O \to NO \tag{13.915}$ 

The bond in the nitric oxide radical comprises a double bond, a  $H_2$ -type molecular orbital 10 (MO) with four paired electrons. The force balance equation and radius  $r_7$  of the 2p shell of N is derived in the Seven-Electron Atoms section. The force balance equation and radius  $r_8$ of the 2p shell of O is derived in the Eight-Electron Atoms section. With the formation of the  $H_2$ -type MO by the contribution of two 2p electrons from each of the N and O atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the 2s and 15 2p electrons of N and O, and the  $H_2$ -type MO. This force from N and O causes the  $H_2$ type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining N and O electrons decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the configuration of NO is resulting electron 20 reactant atoms. The  $N1s^2O1s^2N2s^2O2s^2N2p^1O2p^2\sigma_{N,0}^4$  where  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

Nitric oxide is predicted to be weakly paramagnetic in agreement with observations [42].

### FORCE BALANCE OF THE 2p SHELL OF THE NITROGEN ATOM OF 5 THE NITRIC OXIDE RADICAL

For the N atom, force balance for the outermost 2p electron of NO (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 5 and the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central 10 Coulomb force on the outer-most 2p shell electron of NO (electron 5) due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_s^2} \mathbf{i}_{\mathbf{r}} \tag{13.917}$$

for  $r > r_4$ . The 2p shell possess a +2 external electric field given by Eq. (10.92) for  $r > r_5$ . The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of N in NO are the same as those of N in the nitrogen molecule with  $r_5$  replacing  $r_6$  and with an increase of the central field by an integer. The diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the p-orbital contribution is given by Eq. (13.622) with  $r_5$  replacing  $r_6$ :

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right) \frac{\hbar^2}{4m_e r_5^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{\hbar^2}{12m_e r_5^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r$$
 (13.918)

20 And,  $\mathbf{F}_{mag\ 2}$  corresponding to the conserved orbital angular momentum of the three orbitals is

also the same as that of  $N_2$  given by Eq. (13.623) with  $r_5$  replacing  $r_6$ :

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_s^2 r_3} \sqrt{s(s+1)} \mathbf{i_r}$$
 (13.919)

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_5$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +2 outside of its radius follows from Eq. (13.624):

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_5^4} 10 \sqrt{s(s+1)} \mathbf{i}_r$$
 (13.920)

In addition to the N forces  $\mathbf{F}_{ele}$ ,  $\mathbf{F}_{diamagnetic}$ ,  $\mathbf{F}_{mag~2}$ , and  $\mathbf{F}_{diamagnetic~2}$  of NO being the same as  $N_2$  given by Eqs. (13.621-13.624), respectively,  $\mathbf{F}_{ele}$ ,  $\mathbf{F}_{mag~2}$ , and  $\mathbf{F}_{diamagnetic~2}$  are also the same as those of CN (Eqs. (13.820) and (13.822-13.823)). In the  $N_2$  and CN cases, the contribution of a 2p electron from the N atom in the formation of the  $\sigma$  MO gives rise to an additional paramagnetic force on the remaining two 2p electrons that pair. However, the force,  $\mathbf{F}_{mag~3}$ , is absent in NO since the single outer electron is unpaired.

The radius of the 2p shell is calculated by equating the outward centrifugal force to 15 the sum of the electric (Eq. (13.917)) and diamagnetic (Eqs. (13.918) and (13.920)), and paramagnetic (Eq. (13.919)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \begin{pmatrix}
\frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \frac{\hbar^2}{12m_e r_5^2 r_3} \sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_5^2 r_3} \sqrt{s(s+1)} \\
-\left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_5^4 m_e} 10\sqrt{s(s+1)}$$
(13.921)

Substitution of  $v_5 = \frac{\hbar}{m_e r_5}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.921) gives:

$$\frac{\hbar^2}{m_e r_s^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_s^2} - \frac{\hbar^2}{12m_e r_s^2 r_3} \sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_s^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_s^4 m_e} 10\sqrt{\frac{3}{4}}$$
(13.922)

The quadratic equation corresponding to Eq. (13.922) is

20

$$r_{5}^{2} - \frac{\frac{\hbar^{2}}{m_{e}}}{\left(\frac{(Z-4)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} r_{5} - \frac{\frac{\hbar^{2}}{m_{e}}\left[\frac{Z-5}{Z-4}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_{3}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-4)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} = 0$$
(13.923)

The solution of Eq. (13.923) using the quadratic formula is:

$$\frac{a_{0}}{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{\pm}} + \frac{20\sqrt{3}\left(\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

$$r_{5} = \frac{2}{2}$$

$$(13.924)$$

 $r_3$  in units of  $a_0$ 

5 The positive root of Eq. (13.924) must be taken in order that  $r_5 > 0$ . Substitution of

$$r_3 = 0.69385$$
 (Eq. (10.62) with  $Z = 7$ ) into Eq. (13.924) gives
$$r_5 = 0.74841a_0$$
 (13.925)

### FORCE BALANCE OF THE 2p SHELL OF THE OXYGEN ATOM OF THE 10 NITRIC OXIDE RADICAL

For the O atom, force balance for the outermost 2p electron of NO (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other 2p electron as well as the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron 15 Atoms section. The central Coulomb force on the outer-most 2p shell electron of NO (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_e^2} \mathbf{i_r} \tag{13.926}$$

for  $r > r_5$ . The 2p shell possess an external electric field of +2 given by Eq. (10.92) for  $r > r_6$ . The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the p-orbital contribution is given by:

5 
$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right) \frac{\hbar^2}{4m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r$$
 (13.927)

And,  $F_{mog\ 2}$  corresponding to the conserved spin and orbital angular momentum given by Eqs. (10.157) and (13.670) is

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{2\hbar^2}{m_r r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
 (13.928)

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_6$  gives rise to 10 a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10\sqrt{s(s+1)} \mathbf{i_r}$$
 (13.929)

In addition, the contribution of two 2p electrons in the formation of the  $\sigma$  MO gives rise to a paramagnetic force on the remaining paired 2p electrons. The force  $\mathbf{F}_{mag 3}$  is given 15 by Eq. (13.625) wherein the radius is  $r_6$ :

$$\mathbf{F}_{\text{mag 3}} = \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}}$$
 (13.930)

The radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.926)) and diamagnetic (Eqs. (13.927) and (13.929)), and paramagnetic (Eqs. (13.928) and (13.930)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \frac{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3\hbar^2}{r_6^4 m_e} 10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)}\right)$$
(13.931)

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (13.931) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3} \sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10\sqrt{\frac{3}{4}}$$

(13.932)

The quadratic equation corresponding to Eq. (13.932) is

$$r_{6}^{2} - \frac{\frac{\hbar^{2}}{m_{e}} \left(1 - \frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z - 5)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{2}{12} - \frac{2}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} r_{6} - \frac{\frac{\hbar^{2}}{m_{e}} \left[\frac{Z - 6}{Z - 5}\right] \left(1 - \frac{\sqrt{2}}{2}\right)r_{3}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z - 5)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{2}{12} - \frac{2}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} = 0$$
(13.933)

The solution of Eq. (13.933) using the quadratic formula is:

$$a_{0}\left(1-\frac{\sqrt{3}}{8}\right)$$

$$\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{\pm}a_{0}$$

$$+\frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

$$r_{6} = \frac{20\sqrt{3}\left(\frac{Z-6}{Z-5}\right)\left(1-\frac{\sqrt{2}}{2}\right)r_{3}}{2r_{3}}$$

$$(13.934)$$

 $r_3$  in units of  $a_0$ 

The positive root of Eq. (13.934) must be taken in order that  $r_6 > 0$ . Substitution of  $\frac{r_3}{a_0} = 0.59020$  (Eq. (10.62) with Z = 8) into Eq. (13.934) gives

$$r_6 = 0.70460a_0 \tag{13.935}$$

# 10 ENERGIES OF THE 2p SHELLS OF THE NITROGEN ATOM AND OXYGEN ATOM OF THE NITRIC OXIDE RADICAL

With the formation of the  $H_2$ -type MO by the contribution of two 2p electrons from each of the N and O atoms, the total energy of the NO molecule, which is subtracted from the sum of the energies of the nitrogen and oxygen atoms to determine the bond energy, is increased by the ionization energies of  $N^+$  and  $O^+$  given by Eqs. (10.132-10.133) and (10.152-10.153), respectively. Experimentally, the energies are [6]

$$E(ionization; N^+) = 29.6013 \ eV$$
 (13.936)

$$E(ionization; O^{+}) = 35.11730 \, eV$$
 (13.937)

In addition, the central forces on the 2p shells of the N and O atoms are increased

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with the formation of the  $\sigma$  MO which reduces each shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the N and O atoms at the new radii are calculated and added to the ionization energies of  $N^+$  and  $O^+$ , and the energy of the  $\sigma$  MO to give the total energy of NO. Then, the bond energy is determined from the total 5 NO energy.

The radius  $r_7$  of the nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084a_0 \tag{13.938}$$

Using the initial radius  $r_7$  of the N atom and the final radius  $r_5$  of the N2p shell (Eq. (13.925)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(N,2p)$  of the Coulombic energy change of the N2p electrons of the N atom is determined using Eq. (10.102):

$$E_{T}(N,2p) = -\sum_{n=4}^{4} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{s}} - \frac{1}{r_{\gamma}}\right)$$

$$= -(13.60580 \ eV)(0.26186)(3)$$

$$= -10.68853 \ eV$$
(13.939)

The radius  $r_8$  of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 {(13.940)}$$

Using the initial radius  $r_8$  of the O atom and the final radius  $r_6$  of the O2p shell (Eq. (13.935)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(O,2p)$  of the Coulombic energy change of the O2p electrons of the O atom is determined using Eq. (10.102):

$$E_{T}(O,2p) = -\sum_{n=4}^{5} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{6}} - \frac{1}{r_{8}}\right)$$

$$= -\left(13.60580 \, eV\right) \left(0.41925\right) \left(3+4\right)$$

$$= -39.92918 \, eV$$
(13.941)

20

#### FORCE BALANCE OF THE $\sigma$ MO OF THE NITRIC OXIDE RADICAL

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having +2e at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having +e at each focus. The diamagnetic force  $\mathbf{F}_{diamagneticMO1}$  for 25 the  $\sigma$ -MO of the NO molecule due to the two paired electrons in the O2p shell is given by

Eq. (13.633) with  $n_e = 2$ :

$$\mathbf{F}_{diamagneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi} \tag{13.942}$$

 $\mathbf{F}_{diamagneticMO2}$  of the nitric oxide radical comprising nitrogen with charge  $Z_1 = 7$  and  $|L_1| = \hbar$  and  $|L_2| = \sqrt{\frac{3}{4}}\hbar$  and oxygen with  $Z_2 = 8$  and  $|L_3| = \hbar$  is given by the corresponding sum of the

5 contributions. Using Eq. (13.835),  $\mathbf{F}_{dlamagneticMO2}$  for NO is

$$\mathbf{F}_{diamagneticMO2} = \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$
(13.943)

The general force balance equation for the  $\sigma$ -MO of the nitric oxide radical given by Eqs. (11.200), (13.633-13.634), and (13.942-13.943) is the same as that of CN (Eq. (13.836)):

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.944}$$

10 
$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D - \left( \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D$$
 (13.945)

$$\left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D$$
(13.946)

$$a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) a_0 \tag{13.947}$$

Substitution of  $Z_1 = 7$  and  $Z_2 = 8$  into Eq. (13.947) gives

$$a = 2.39158a_0 = 1.26557 \ X \ 10^{-10} \ m \tag{13.948}$$

15 Substitution of Eq. (13.948) into Eq. (11.79) is

$$c' = 1.09352a_0 = 5.78666 \ X \ 10^{-11} \ m \tag{13.949}$$

The internuclear distance given by multiplying Eq. (13.949) by two is

$$2c' = 2.18704a_0 = 1.15733 \times 10^{-10} m \tag{13.950}$$

The experimental bond distance is [28]

$$2c' = 1.15077 X 10^{-10} m ag{13.951}$$

Substitution of Eqs. (13.948-13.949) into Eq. (11.80) is

$$b = c = 2.12693a_0 = 1.12552 \times 10^{-10} m$$
 (13.952)

Substitution of Eqs. (13.948-13.949) into Eq. (11.67) is

$$e = 0.45724 \tag{13.953}$$

(10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)),  $N2p = 0.74841a_0$  (Eq. (13.925)),  $O1s = 0.12739a_0$  10 (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = 0.70460a_0$  (Eq. (13.935)) shells and the parameters of the  $\sigma$  MO of NO given by Eqs. (13.3-13.4), (13.948-13.950), and (13.952-13.953), the dimensional diagram and charge-density of the NO MO are shown in Figures 31 and 32, respectively.

Using the electron configuration of NO (Eq. (13.916)), the radii of the  $N1s = 0.14605a_0$  (Eq.

### 15 SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE NITRIC OXIDE RADICAL

The energies of the NO  $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (13.948-13.949) and (13.952)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$  except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied 20 by two due to the  $\sigma$ -MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -98.30623 \ eV$$
 (13.954)

$$V_p = 2^2 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 49.76880 \ eV \tag{13.955}$$

$$T = 2\frac{\hbar^2}{2m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 10.27631 \text{ eV}$$
 (13.956)

$$V_{m} = 2^{2} \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} = -10.27631 \ eV$$
 (13.957)

$$E_T = V_e + T + V_m + V_p \tag{13.958}$$

Substitution of Eqs. (11.79) and (13.954-13.957) into Eq. (13.958) gives

$$E_{T}(NO,\sigma) = \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left( 8\ln\frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 4 \right) = -48.53743 \ eV$$
 (13.959)

where  $E_T(NO,\sigma)$  is the total energy of the  $\sigma$  MO of NO. The total energy of NO,  $E_T(NO)$ , is given by the sum of  $E(ionization; N^+)$ , the energy of the second electron of nitrogen (Eq. (13.936)) donated to the double bond,  $E(ionization; O^+)$ , the energy of the second electron of oxygen (Eq. (13.937)) donated to the double bond,  $E_T(N,2p)$ , the N2p AO contribution due to the decrease in radius with bond formation (Eq. (13.939)),  $E_T(O,2p)$ , the O2p AO contribution due to the decrease in radius with bond formation (Eq. (13.941)), and  $E_T(NO,\sigma)$ , the  $\sigma$  MO contribution given by Eq. (13.959):

$$E_{T}(NO) = \begin{pmatrix} E(ionization; N^{+}) + E(ionization; O^{+}) \\ + E_{T}(N, 2p) + E_{T}(O, 2p) + E_{T}(NO, \sigma) \end{pmatrix}$$

$$= \begin{pmatrix} 29.6013 \ eV + 35.11730 \ eV \\ -10.68853 \ eV - 39.92918 \ eV - 48.53743 \ eV \end{pmatrix}$$

$$= -34.43653 \ eV$$
(13.960)

10

#### VIBRATION OF NO

The vibrational energy levels of NO may be solved by determining the Morse potential curve from the energy relationships for the transition from a N atom and O atom whose parameters are given by Eqs. (10.134-10.143) and (10.154-10.163), respectively, to a N atom whose parameter  $r_5$  is given by Eq. (13.925), an O atom whose parameter  $r_6$  is given by Eq. (13.935), and the  $\sigma$  MO whose parameters are given by Eqs. (13.948-13.950) and (13.952.-13.953). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

### THE DOPPLER ENERGY TERMS OF THE NITRIC OXIDE RADICAL

The equations of the radiation reaction force of nitric oxide are the same as those of  $H_2$  with the substitution of the NO parameters except that there is a factor of four increase in the central force in Eq. (11.231) due to the double bond. Using Eqs. (11.231-11.233) and 5 (13.901), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{4e^2}{4\pi\varepsilon_0 a^3}} = 2.23557 \, X \, 10^{16} \, rad/s \tag{13.961}$$

where a is given by Eq. (13.948). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\vec{E}_{K} = \hbar\omega = \hbar 2.23557 \, X \, 10^{16} \, rad \, / \, s = 14.71493 \, eV$$
 (13.962)

10 In Eq. (11.181), substitution of  $E_T(NO)$  for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (13.962) for  $\overline{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -34.43653 \ eV \sqrt{\frac{2e(14.71493 \ eV)}{m_e c^2}} = -0.26134 \ eV$$
 (13.963)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the NO MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (13.963) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental NO  $\omega_e$  of 1904.20 cm<sup>-1</sup> (0.23609 eV) [28] for

20  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}'_{osc}(NO)$  per bond is

$$\overline{E}'_{osc}(NO) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(13.964)

$$\overline{E}'_{osc}(NO) = -0.26134 \ eV + \frac{1}{2}(0.23609 \ eV) = -0.14329 \ eV \tag{13.965}$$

Since the  $\sigma$  MO bond is a double bond with twice a many electrons as a single bond,  $\overline{E}'_{osc}(NO)$  is multiplied by two to give

25 
$$\overline{E}_{osc}(NO) = -0.28658 \ eV$$
 (13.966)

TOTAL AND BOND ENERGIES OF THE NITRIC OXIDE RADICAL  $E_{T+asc}(NO)$ , the total energy of NO including the Doppler term, is given by the sum of  $E_{T}(NO)$  (Eq. (13.960)) and  $\overline{E}_{asc}(NO)$  given by Eq. (13.966):

$$E_{T+osc}(NO) = \begin{pmatrix} V_e + T + V_m + V_p + E(ionization; N^+) + E(ionization; O^+) \\ + E_T(N, 2p) + E_T(O, 2p) + \overline{E}_{osc}(NO) \end{pmatrix}$$

$$= \begin{pmatrix} E_T(NO, \sigma) + E(ionization; N^+) + E(ionization; O^+) \\ + E_T(N, 2p) + E_T(O, 2p) + \overline{E}_{osc}(NO) \end{pmatrix}$$

$$= E_T(NO) + \overline{E}_{osc}(NO)$$
(13.967)

$$E_{T+osc}(NO) = \begin{cases} \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{2} - 4\right) \\ +E(ionization; N^+) + E(ionization; O^+) \\ -\sum_{N,n=4}^4 \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_s} - \frac{1}{r_\eta}\right) -\sum_{O,n=4}^5 \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_6} - \frac{1}{r_8}\right) \end{cases}$$

$$= -34.43653 \ eV - 2(0.26134 \ eV) + 2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$(13.968)$$

From Eqs. (13.966-13.968), the total energy of the NO MO is

$$E_{T+osc}(NO) = -34.43653 \ eV + \overline{E}_{osc}(NO)$$

$$= -34.43653 \ eV + (-0.28658)$$

$$= -34.72312 \ eV$$
(13.969)

where the experimental  $\omega_e$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

The NO bond dissociation energy,  $E_D(NO)$ , is given by the difference between the sum of the energies of the N and O atoms and  $E_{T+osc}(NO)$ :

$$E_D(NO) = E(N) + E(O) - E_{T+osc}(NO)$$
 (13.970)

where the energy of a nitrogen atom is [6]

$$E(N) = -14.53414 \, eV \tag{13.871}$$

and the energy of an oxygen atom is [6]

$$E(O) = -13.61806 \, eV \tag{13.972}$$

Thus, the NO bond dissociation energy,  $E_D(NO)$ , given by Eqs. (13.969-13.972) is

$$E_D(NO) = -(14.53414 \ eV + 13.61806 \ eV) - E_{T+osc}(NO)$$

$$= -28.15220 \ eV - (-34.72312 \ eV)$$

$$= 6.57092 \ eV$$
(13.973)

The experimental NO bond dissociation energy is [49]

$$E_{D298}(NO) = 6.5353 \text{ eV} {13.974}$$

The results of the determination of bond parameters of NO are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations 10 containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Table 13.1. The calculated and experimental bond parameters of  $H_3^+$ ,  $D_3^+$ , OH, OD,  $H_2O$ ,  $D_2O$ , NH, ND,  $NH_2$ ,  $ND_2$ ,  $NH_3$ ,  $ND_3$ , CH, CD,  $CH_2$ ,  $CH_3$ ,  $CH_4$ ,  $N_2$ ,  $O_2$ ,  $F_2$ ,  $Cl_2$ , 15 CN, CO, and NO.

Parameter	Calculated	Experimental	Ref. for Exp
H <sub>3</sub> <sup>+</sup> Bond Energy	4.373 eV	4.373 eV	8
D <sub>3</sub> <sup>+</sup> Bond Energy	4.374 eV		
OH Bond Energy	4.4104 eV	4.4117 eV	22
OD Bond Energy	4.4687 eV	4.454 eV	23
OH Bond Length	0.971651 Å	0.971 Å	13
OD Bond Length	0.971651 Å	0.971 Å	13
OH Vibrational Energy	0.4367 eV	0.4424 eV	16-17
OD Vibrational Energy	0.3219 eV	0.3263 eV	16-17
OH ω <sub>ε</sub>	3696.38 cm <sup>-1</sup>	3735.21 cm <sup>-1</sup>	14
OD $\omega_e$	2689.51 cm <sup>-1</sup>	2720.9 cm <sup>-1</sup>	14
$OH \omega_e x_e$	87.18 cm <sup>-1</sup>	$82.81 \ cm^{-1}$	14
$OD \omega_e x_e$	46.75 cm <sup>-1</sup>	44.2 cm <sup>-1</sup>	14
OH B,	18.835 cm <sup>-1</sup>	18.871 cm <sup>-1</sup>	14

Parameter	291 Calculated	Experimental	Ref. for Exp.
OD B <sub>e</sub>	9.971 cm <sup>-1</sup>	10.01 cm <sup>-1</sup>	14
$H_2O$ Bond Energy	5.1059 eV	5.0991 eV	26
$D_2O$ Bond Energy	5.178 eV	5.191 eV	31-32
$H_2O$ $O-H$ Bond Length	0.971574 Å	0.970 ± 0.005 Å	23
$D_2O O - D$ Bond Length	0.971574 Å	$0.970 \pm 0.005  \text{\AA}$	23
$H_2O$ $H-H$ Distance	1.552 Å	1.55 ± 0.01 Å	13
$D_2O$ $D-D$ Distance	1.552 Å	$1.55 \pm 0.01  \text{\AA}$	13
$H_2O$ Bond Angle	106°	106°	23
$D_2O$ Bond Angle	. 106°	106°	23
NH Bond Energy	3.47530 eV	3.47 eV	30
ND Bond Energy	3.52556 eV	3.5134 eV	31
NH Bond Length	1.04262 Å	1.0362 Å	28
ND Bond Length	1.04262 Å	1.0361 Å	28
NH Vibrational Energy	0.38581 eV	0.38752 eV	28
ND Vibrational Energy	0.28583 eV	0.28690 eV	28
$NH \omega_e$	3284.58 <i>cm</i> <sup>-1</sup>	3282.3 cm <sup>-1</sup>	28
$ND \omega_{\epsilon}$	$2398.72 \ cm^{-1}$	2398 cm <sup>-1</sup>	28
$NH \omega_e x_e$	$86.37 \ cm^{-1}$	78.4 cm <sup>-1</sup>	28
$ND \omega_e x_e$	$47.40 \ cm^{-1}$	42 $cm^{-1}$	28
$NH$ $B_e$	16.495 cm <sup>-1</sup>	16.993 cm <sup>-1</sup>	. 28
$ND B_e$	$8.797 \ cm^{-1}$	8.7913 cm <sup>-1</sup>	28
NH <sub>2</sub> Bond Energy	3.9323 eV	3.9461 eV	35
ND <sub>2</sub> Bond Energy	3.9401 eV	3.9362 eV	33-35
NH <sub>2</sub> Bond Length	1.04262 Å	1.0240 Å	32
$ND_2$ Bond Length	1.04262 Å		
NH <sub>2</sub> Bond Angle	105.97	103.3°	32
$ND_2$ Bond Angle	105.97		
NH <sub>3</sub> Bond Energy	4.57913 eV	4.60155 eV	37
ND <sub>3</sub> Bond Energy	4.64499 eV	4.71252 eV	37

^	2
٠,	4,

Parameter	292 Calculated	Experimental	Ref. for Exp.
NH <sub>3</sub> Bond Length	1.0368 Å	1.012 Å	32
ND <sub>3</sub> Bond Length	1.0368 Å		
NH <sub>3</sub> Bond Angle	106.67	106.67°	36
ND <sub>3</sub> Bond Angle	106.67	106.70	36
CH Bond Energy	3.47404 eV	3.47 eV	14
CD Bond Bnergy	3.51673 eV	3.52 eV	14
CH Bond Length	1.1183 Å	1.1198 Å	14
CD Bond Length	1,1183 Å	1.118 Å	14
CH Vibrational Energy	0.33879 eV	0.33885 eV	14
CD Vibrational Energy	0.25173 eV	0.25189 eV	14 .
$CH \omega_e$	2865.86 cm <sup>-1</sup>	2861.6 cm <sup>-1</sup>	14
$CD \omega_{\epsilon}$	$2102.97 \ cm^{-1}$	2101.0 cm <sup>-1</sup>	14 .
CH $\omega_e x_e$	66.624 cm <sup>-1</sup>	64.3 cm <sup>-1</sup>	14
$CD \omega_{\epsilon} x_{\epsilon}$	$36.335 \ cm^{-1}$	34.7 cm <sup>-1</sup>	14
CH B <sub>e</sub>	14.498 cm <sup>-1</sup>	$14.457 \ cm^{-1}$	14
$CD B_e$	7.807 $cm^{-1}$	$7.808 \ cm^{-1}$	14
$CH_2$ Bond Energy	4.36968 eV	4.33064 eV	39
$CH_2$ Bond Length	1.1067 Å	1.111 Å	38
$CH_2$ Bond Angle	100.22	102.4°	38
$CH_3$ Bond Energy	4.70075 eV	4.72444 eV	40
$CH_3$ Bond Length	1.1029 Å	1.079 Å	38
CH <sub>3</sub> Bond Angle	100.70°		
$CH_{\scriptscriptstyle 4}$ Bond Energy	4.4900 eV	4.48464 eV	40
$CH_4$ Bond Length	1.1010 Å	1.087 Å	41
CH <sub>4</sub> Bond Angle	109.5°	109.5°	41
$N_2$ Bond Energy.	9.71181 eV	9.756 eV	43
$N_2$ Bond Length	1.0955 Å	1.094 Å	<b>43</b>
$O_2$ Bond Energy	5.10711 eV	5.11665 eV	46
$O_2$ Bond Length	1.20862 Å	1.20752 Å	28

Parameter	Calculated	Experimental	Ref. for Exp.
$F_2$ Bond Energy	1.62168 eV	1.606 eV	48
$F_{\rm 2}$ Bond Length	1.41114 Å	1.41193 Å	28
Cl <sub>2</sub> Bond Energy	2.52236 eV	2.51412 eV	49
${\it Cl}_2$ Bond Length	1.988 Å	1.988 Å	28
$Cl_2$ $\omega_e$	$538.52 \ cm^{-1}$	559.7 cm <sup>-1</sup>	28
$Cl_2 \ \omega_e x_e$	3.41 cm <sup>-1</sup>	$2.68 \ cm^{-1}$	28
Cl <sub>2</sub> B <sub>e</sub>	$0.2420 \ cm^{-1}$	0.2440 cm <sup>-1</sup>	28
CN Bond Energy	7.77526 eV	7.7731 eV	50
CN Bond Length	1.17231 Å	1.17181 Å	28
CO Bond Energy	11.16652 eV	11.15696 eV	49 .
CO Bond Length	1.13290 Å	1.12823 Å	28
NO Bond Energy	6.57092 eV	6.5353 eV	49
NO Bond Length	1.15733 Å	1. <b>15077</b> Å	28

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### **Section III**

### MORE POLYATOMIC MOLECULES AND HYDROCARBONS

Additional polyatomic molecules can be solved using the same principles as those used to 5 solve hydrogen molecular ions and molecules wherein the hydrogen molecular orbitals (MOs) and hydrogen atomic orbitals serve as basis functions for the MOs. The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron 10 angular momentum of  $\hbar$ . Energy of the MO must be matched to that of the outermost atomic orbital of a bonding heteroatom in the case where a minimum energy is achieved with a direct bond to the AO. Alternatively, the MO is continuous with the AO containing paired electrons that do not participate in the bond. Rather, they only provide a means for the energy matched MO to form a continuous equipotential energy surface. In the case that an independent MO is 15 formed, the AO force balance causes the remaining electrons to be at lower energy and a smaller radius. In another case, the atomic orbital may hybridize in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. Representative cases were solved. 20 Specifically, the results of the determination of bond parameters of carbon dioxide (CO2), nitrogen dioxide ( $NO_2$ ), ethane ( $CH_3CH_3$ ), ethylene ( $CH_2CH_2$ ), acetylene (CHCH), benzene  $(C_6H_6)$ , propane  $(C_3H_8)$ , butane  $(C_4H_{10})$ , pentane  $(C_5H_{12})$ , hexane  $(C_6H_{14})$ , heptane  $(C_7H_{16})$ , octane  $(C_8H_{18})$ , nonane  $(C_9H_{20})$ , decane  $(C_{10}H_{22})$ , undecane  $(C_{11}H_{24})$ , dodecane  $(C_{12}H_{26})$ , and octadecane  $(C_{18}H_{38})$  are given in Table 14.1. The calculated results 25 are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

#### CARBON DIOXIDE MOLECULE

30 The carbon dioxide molecule can be formed by the reaction of carbon monoxide and an oxygen atom:

$$CO + O \rightarrow CO_2$$
 (14.1)

Each equivalent bond in the carbon dioxide molecule comprises a double bond that is energy-matched to the filled C2s orbital. Each such bond comprises 75% of a  $H_2$ -type MO with four paired electrons as a basis set such that three electrons can be assigned to each C=O bond. Thus, the two C2p electrons combine with the four O2p electrons, two from each O, as a linear combination to form the two C=O bonds of  $CO_2$ . The force balance equation and radius  $r_8$  of the 2p shell of O is derived in the Eight-Electron Atoms section. With the formation of the  $H_2$ -type MOs by the contribution of two 2p electrons from each of the two O atoms, a factor of two increase of the central field on the remaining O2p electrons arises. The resulting increased Coulombic as well as magnetic central forces decrease the radii of the O2p shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $CO_2$  is  $C1s^2O_11s^2O_21s^2C2s^2O_12s^2O_22s^2O_12p^2O_22p^2O_{O_2,C,O_1}$  where the subscripts designate the O atom, 1 or 2,  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

$$\begin{array}{ccc}
 & 1s \text{ state} \\
 & \uparrow \downarrow & \uparrow \downarrow \\
 O & C & O
\end{array}$$

 $\sigma$  state

Carbon dioxide is predicted to be diamagnetic in agreement with observations [1].

# FORCE BALANCE OF THE 2p SHELL OF THE OXYGEN ATOM OF THE CARBON DIOXIDE MOLECULE

20 For each O atom, force balance for the outermost 2p electron of  $CO_2$  (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due

to interactions between electron 6 and the other 2p electrons as well as the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most 2p shell electron of CO (electron 6) due to the nucleus and the inner five electrons is given by Eq. 5 (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} \mathbf{i_r} \tag{14.3}$$

for  $r > r_5$ . The 2p shell possess a +2 external electric field given by Eq. (10.92) for  $r > r_6$ . The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the p-orbital contribution is 10 given by:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right) \frac{\hbar^2}{4m_e r_o^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_o^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r$$
 (14.4)

where s = 1/2. And,  $\mathbf{F}_{mag 2}$  corresponding to the conserved spin and orbital angular momentum given by Eq. (10.157) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{2\hbar^2}{m_e r_6^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r \tag{14.5}$$

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_6$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is:

$$\mathbf{F}_{dicanagnetic 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10\sqrt{s(s+1)} \mathbf{i}_r$$
 (14.6)

The radius of the 2p shell is calculated by equating the outward centrifugal force to 20 the sum of the electric (Eq. (14.3)) and diamagnetic (Eqs. (14.4) and (14.6)), and paramagnetic (Eq. (14.5)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10\sqrt{s(s+1)}$$
(14.7)

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (14.7) gives:

$$\frac{\hbar^2}{m_e r_6^3} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10\sqrt{\frac{3}{4}}$$
(14.8)

The quadratic equation corresponding to Eq. (14.8) is

$$r_{6}^{2} - \frac{\frac{\hbar^{2}}{m_{e}}}{\left(\frac{(Z-5)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{2}{12} - \frac{2}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} r_{6} - \frac{\frac{\hbar^{2}}{m_{e}}\left[\frac{Z-6}{Z-5}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_{3}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{2}{12} - \frac{2}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} = 0$$
(14.9)

5 The solution of Eq. (14.9) using the quadratic formula is:

$$\frac{a_{0}}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{\pm}a_{0}} + \frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

$$r_{6} = \frac{2}{2}$$
(14.10)

 $r_3$  in units of  $a_0$ 

The positive root of Eq. (14.10) must be taken in order that  $r_6 > 0$ . Substitution of  $\frac{r_3}{a_0} = 0.59020$  (Eq. (10.62) with Z = 8) into Eq. (14.10) gives

$$r_6 = 0.74776a_0 \tag{14.11}$$

10

ENERGIES OF THE 2s AND 2p SHELLS OF THE CARBON ATOM AND THE 2p SHELL OF THE OXYGEN ATOMS OF THE CARBON DIOXIDE MOLECULE

Consider the determination of the total energy of  $CO_2$  from the reaction of a carbon atom 15 with two oxygen atoms. With the formation of the  $H_2$ -type MO by the contribution of two 2p electrons from the C atom, the remaining outer-shell atomic electrons comprise the 2s electrons which are unchanged by bonding with two oxygen atoms. However, the total energy of the  $CO_2$  molecule, which is subtracted from the sum of the energies of the oxygen atom and carbon monoxide molecule to determine the O-CO bond energy, is increased by

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the ionization energies of C,  $C^+$ , O, and  $2O^+$  given by Eqs. (14.12-14.15), respectively. Experimentally, the energies are [2]

$$E(ionization; C) = 11.26030 \, eV$$
 (14.12)

$$E(ionization; C^+) = 24.38332 \, eV$$
 (14.13)

5 
$$E(ionization; O) = 13.61806 eV$$
 (14.14)

$$E(ionization; O^{+}) = 35.11730 \, eV$$
 (14.15)

In addition, the central forces on the 2p shell of the O atom are increased with the formation of the  $\sigma$  MO which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of each O atom at the new radius are calculated and added to the ionization energies of C,  $C^+$ , O, and  $2O^+$ , and the energy of the  $\sigma$  MO to give the total energy of  $CO_2$ . Then, the bond energy is determined from the total  $CO_2$  energy.

The radius  $r_8$  of each oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0$$
 (14.16)

Using the initial radius  $r_8$  of each O atom and the final radius  $r_6$  of the O2p shell (Eq. (14.11)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(O,2p)$  of the Coulombic energy change of the O2p electrons of each O atom is determined using Eq. (10.102):

$$E_{T}(O,2p) = -\sum_{n=4}^{5} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{6}} - \frac{1}{r_{8}}\right)$$

$$= -\left(13.60580 \ eV\right) \left(0.33733\right) \left(3+4\right)$$

$$= -32.12759 \ eV$$
(14.17)

20

## FORCE BALANCE OF THE $\sigma$ MO OF THE CARBON DIOXIDE MOLECULE

As in the case of  $H_2$ , the  $\sigma$  MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the C atom for distances shorter than the radius of the C2s shell; nor, can it extend into the O atom for distances shorter than the radius of the O2p shell. Thus, the MO surface of each C=O bond comprises a prolate spheroid that bridges and is continuous with the 2s and 2p shells of the O and C atoms whose nuclei serve as the foci. The energy of each prolate spheroid is matched to that of the C2s and C2p shells.

As in the case of previous examples of energy-matched MOs such as OH and NH, the C = O-bond MO must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. However, the paired electrons of the C2s and O2p shells are not involved in bonding. Rather, the AOs permit a continuous surface 5 comprising the two C = O-bond MOs having six paired electrons, two from each of the Cand the two O atoms:

$$2(0.75 H_2 MO) \rightarrow CO_2 MO$$
 (14.18)

10 The force balance of the CO<sub>2</sub> MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.18) and the energy matching condition between the carbon and oxygen components of the MO.

Similar to the OH and  $H_2O$  cases given by Eqs. (13.57) and (13.162), the  $H_2$ -type ellipsoidal MO comprises 75% of the  $CO_2$  MO; so, the electron charge density in Eq. (11.65) 15 is given by -0.75e. Thus, k' of the each  $H_2$ -type-ellipsoidal-MO component of the  $CO_2$ MO is given by Eq. (13.59). The distance from the origin of each C = O-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C = O-bond MO b = c given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). Then, the solution of the semimajor 20 axis a allows for the solution of the other axes of the prolate spheroidal and eccentricity of the CO<sub>2</sub> MO.

The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of the  $CO_2$   $\sigma$  MO are the same as those of OH given by Eqs. (13.67-13.73), except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to each  $\sigma$ -MO double 25 bond:

$$E_T(C=O,\sigma) = -\frac{4e^2}{8\pi\varepsilon_0 c'} \left[ \left(\frac{3}{2}\right) \ln \frac{a+c'}{a-c'} - 1 \right]$$
(14.19)

where  $E_T(C=O,\sigma)$  is the total energy of each C=O  $\sigma$  MO of  $CO_2$ . The total energy of a  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75). A minimum energy is obtained when each double bond of the  $\sigma$  MO of  $CO_2$  comprises the energy equivalent of 30 four  $H_2$ -type ellipsoidal MOs. For each C = O bond to match the energy of the C2s orbital,

the ionization energy of C and  $C^+$  (Eqs. (14.12-14.13)) must be added for each bond of the double bond. Thus, the total energy of each C = O-bond MOs is

$$E_{T}(C=O,\sigma) = 2 \left( 2 \left( -\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - \sqrt{2} \right] \right) + E(ionization; C) + E(ionization; C^{+}) \right)$$

$$= 2 \left( 2 \left( -31.63536831 \, eV \right) + 11.26030 \, eV + 24.38332 \, eV \right)$$

$$= -55.25423 \, eV$$
(14.20)

 $E_T(C=O,\sigma)$  given by Eq. (14.19) is set equal to Eq. (14.20):

$$5 \qquad \frac{4e^2}{8\pi\varepsilon_0 c'} \left[ \left( \frac{3}{2} \right) \ln \frac{a+c'}{a-c'} - 1 \right] = e55.25423 \ eV$$
 (14.21)

From the energy relationship given by Eq. (14.21) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CO<sub>2</sub> MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.21) gives

$$E_{T}(C=O,\sigma) = \frac{4e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{2aa_{0}}{3}}} \left[ \left(\frac{3}{2}\right) \ln \frac{a + \sqrt{\frac{2aa_{0}}{3}}}{a - \sqrt{\frac{2aa_{0}}{3}}} - 1 \right] = e55.25423 \ eV$$
 (14.22)

10 The most convenient way to solve Eq. (14.22) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.80703a_0 = 9.56239 X 10^{-11} m ag{14.23}$$

Substitution of Eq. (14.23) into Eq. (13.60) is

$$c' = 1.09758a_0 = 5.80815 X 10^{-11} m ag{14.24}$$

15 The internuclear distance given by multiplying Eq. (14.24) by two is

$$2c' = 2.19516a_0 = 1.16163 \ X \ 10^{-10} \ m \tag{14.25}$$

The experimental bond distance is [3]

$$2c' = 1.1600 X 10^{-10} m ag{14.26}$$

Substitution of Eqs. (14.23-14.24) into Eq. (13.62) is

20 
$$b = c = 1.43550a_0 = 7.59636 \times 10^{-11} m$$
 (14.27)

Substitution of Eqs. (14.23-14.24) into Eq. (13.63) is

$$e = 0.60740 \tag{14.28}$$

The C and O nuclei comprise the foci of each  $H_2$ -type ellipsoidal MO defined as O = C = O. Consider the left-hand C = O bond of the two equivalent bonds in the absence

of the right-hand bond. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the C2s AO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_4 = 0.84317a_0$  is the radius of the C2s shell. Substitution of Eqs. (14.23-14.24) into Eq. (13.261) gives

$$\theta' = 54.53^{\circ}$$
 (14.29)

Then, the angle  $\theta_{C2s40}$  the radial vector of the C2s AO makes with the internuclear axis is

$$\theta_{C2540} = 180^{\circ} - 54.53^{\circ} = 125.47^{\circ} \tag{14.30}$$

as shown in Figure 33. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle ωt = θ<sub>H,MO</sub>
10 between the internuclear axis and the point of intersection of the H<sub>2</sub>-type ellipsoidal MO with the C2s radial vector obeys the following relationship:

$$r_4 \sin \theta_{C2sAO} = 0.84317 a_0 \sin \theta_{C2sAO} = b \sin \theta_{H_2MO}$$
 (14.31)

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{0.84317a_0 \sin \theta_{C2sMO}}{b} = \sin^{-1} \frac{0.84317a_0 \sin 125.47^{\circ}}{b}$$
 (14.32)

15 with the use of Eq. (14.30). Substitution of Eq. (14.27) into Eq. (14.32) gives

$$\theta_{H,MO} = 28.58^{\circ}$$
 (14.33)

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H,MO} = a\cos\theta_{H,MO} \tag{14.34}$$

20 Substitution of Eqs. (14.23) and (14.33) into Eq. (14.34) gives

$$d_{H_2MO} = 1.58687a_0 = 8.39737 X 10^{-11} m ag{14.35}$$

The distance  $d_{C2MO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C2sAO} = d_{H_2MO} - c' (14.36)$$

25 Substitution of Eqs. (14.24) and (14.35) into Eq. (14.36) gives

$$d_{C2sAO} = 0.48929a_0 = 2.58922 X 10^{-11} m ag{14.37}$$

The C and O nuclei comprise the foci of each  $H_2$ -type ellipsoidal MO defined as O = C = O. Consider the right-hand C = O bond of the two equivalent bonds. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the O2p AO are

given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_6 = 0.74776a_0$  is the radius of the O2p shell. Substitution of Eqs. (14.23-14.24) into Eq. (13.261) gives

$$\theta' = 30.18^{\circ}$$
 (14.38)

5 Then, the angle  $\theta_{O2pAO}$  the radial vector of the O2p AO makes with the internuclear axis is

$$\theta_{O2pAO} = 180^{\circ} - 30.18^{\circ} = 149.82^{\circ} \tag{14.39}$$

as shown in Figure 33. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the O2p radial vector obeys the following relationship:

$$r_6 \sin \theta_{O2\,pAO} = 0.74776 a_0 \sin \theta_{O2\,pAO} = b \sin \theta_{H,MO} \tag{14.40}$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{0.74776a_0 \sin \theta_{O2pAO}}{h} = \sin^{-1} \frac{0.74776a_0 \sin 149.82^{\circ}}{h}$$
(14.41)

with the use of Eq. (14.39). Substitution of Eq. (14.27) into Eq. (14.41) gives

15 
$$\theta_{H_2MO} = 15.18^{\circ}$$
 (14.42)

Then, the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{14.43}$$

Substitution of Eqs. (14.23) and (14.42) into Eq. (14.43) gives

$$d_{H_2MO} = 1.74396a_0 = 9.22862 X 10^{-11} m (14.44)$$

The distance  $d_{O2pAO}$  along the internuclear axis from the origin of each O atom to the point of intersection of the orbitals is given by

$$d_{2pAO} = d_{H_2MO} - c' (14.45)$$

Substitution of Eqs. (14.24) and (14.44) into Eq. (14.45) gives

$$d_{O2pAO} = 0.64637a_0 = 3.42047 X 10^{-11} m (14.46)$$

As shown in Eq. (14.18), each C = O bond comprises a factor of 0.75 of the chargedensity of double that of the  $H_2$ -type ellipsoidal MO. Using the electron configuration of  $CO_2$  (Eq. (14.2)), the radii of the  $C1s = 0.17113a_0$  (Eq. (10.51)),  $C2s = 0.84317a_0$  (Eq. (10.62)),  $O1s = 0.12739a_0$  (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = 0.74776a_0$  (Eq. (14.11)) shells and the parameters of the  $\sigma$  MO of  $CO_2$  given by Eqs. (13.3-13.4), (14.23-14.25), and (14.27-14.28), the dimensional diagram and charge-density of the  $CO_2$  MO are shown in Figures 33 and 34, respectively.

# 5 SUM OF THE ENERGIES OF THE $\sigma$ MO AND THE AOs OF THE CARBON DIOXIDE MOLECULE

The energies of the  $CO_2$   $\sigma$  MO are given by the substitution of the semiprincipal axes (Eqs. (14.23-14.24) and (14.27)) into the energy equations of OH (Eqs. (13.67-13.73)), except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by 10 two due to each  $\sigma$ -MO double bond;

$$V_e = 2^2 \left(\frac{3}{4}\right) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -104.83940 \ eV \tag{14.47}$$

$$V_p = 2^2 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 49.58464 \ eV \tag{14.48}$$

$$T = 2\left(\frac{3}{4}\right) \frac{\hbar^2}{2m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 14.50438 \ eV$$
 (14.49)

$$V_m = 2^2 \left(\frac{3}{4}\right) \frac{-\hbar^2}{4m \, a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -14.50438 \, eV \tag{14.50}$$

15 
$$E_T = V_e + T + V_m + V_p \tag{14.51}$$

Substitution of Eqs. (13.60) and (14.47-14.50) into Eq. (14.51) gives

$$E_{T}(C=O,\sigma) = V_{e} + T + V_{m} + V_{p} = \frac{-4e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{2aa_{0}}{3}}} \left[ \left(\frac{3}{2}\right) \ln \frac{a + \sqrt{\frac{2aa_{0}}{3}}}{a - \sqrt{\frac{2aa_{0}}{3}}} - 1 \right] = -55.25476 \ eV$$
(14.52)

where  $E_T(C=O,\sigma)$  is the total energy of each C=O  $\sigma$  MO of  $CO_2$  given by Eq. (14.19) which is reiteratively matched to Eq. (14.20) within five-significant-figure round off error.

The total energy of  $CO_2$ ,  $E_T(CO_2)$ , is given by the sum of E(ionization; C) and  $E(ionization; C^*)$ , the sum of the energies of the first and second electrons of carbon (Eqs. (14.12-14.13)) donated to each double bond, the sum of E(ionization; O) and two times  $E(ionization; O^*)$ , the energies of the first and second electrons of oxygen (Eqs. (14.14-

14.15)) donated to the double bonds, two times  $E_T(O,2p)$ , the O2p AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.17)), and two times  $E_T(C=O,\sigma)$ , the  $\sigma$  MO contribution given by Eq. (14.22):

$$\begin{split} E_{T}(CO_{2}) &= \begin{pmatrix} E(ionization; \ C) + E(ionization; \ C^{+}) + E(ionization; \ O) \\ + 2E(ionization; \ O^{+}) + 2E_{T}(O,2p) + 2E_{T}(C=O,\sigma) \end{pmatrix} \\ &= \begin{pmatrix} 11.26030 \ eV + 24.38332 \ eV + 13.61806 \ eV \\ + 2(35.11730 \ eV) + 2(-32.12759 \ eV) \end{pmatrix} \\ &= \begin{pmatrix} \frac{4e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{2aa_{0}}{3}}} \left( \frac{3}{2} \ln \frac{a + \sqrt{\frac{2aa_{0}}{3}}}{a - \sqrt{\frac{2aa_{0}}{3}}} - 1 \right) \\ = \begin{pmatrix} 11.26030 \ eV + 24.38332 \ eV + 13.61806 \ eV \\ + 2(35.11730 \ eV) + 2(-32.12759 \ eV) - 2(55.25423 \ eV) \end{pmatrix} \\ &= -55.26841 \ eV \end{split}$$

VIBRATION OF CO2

5

The vibrational energy levels of  $CO_2$  may be solved by determining the Morse potential curve from the energy relationships for the transition from a C atom and two O atoms whose parameters are given by Eqs. (10.115-10.123) and (10.154-10.163), respectively, to a C atom whose parameter  $r_4$  is given by Eq. (10.61), two O atoms whose parameter  $r_6$  is given by Eq. (14.11), and the  $\sigma$   $CO_2$  MO whose parameters are given by Eqs. (14.23-14.25) and (14.27-14.28). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [4] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

THE DOPPLER ENERGY TERMS OF THE CARBON DIOXIDE 20 MOLECULE

The equations of the radiation reaction force of carbon dioxide are the same as those of OH with the substitution of the  $CO_2$  parameters except that there is a factor of four increase in the

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central force in Eq. (13.140) due to the double bond. Using Eqs. (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{4(0.75)e^2}{4\pi\varepsilon_0 b^3}} = 4.16331 \, X \, 10^{16} \, rad/s \tag{14.54}$$

where b is given by Eq. (14.27). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. 5 (11.127)):

$$\overline{E}_K = \hbar \omega = \hbar 4.16331 \, X \, 10^{16} \, rad \, / \, s = 27.40365 \, eV$$
 (14.55)

In Eq. (11.181), substitution of  $E_T(CO_2)/2$  for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.55) for  $\overline{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

10 
$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -27.63421 \ eV \sqrt{\frac{2e(27.40365 \ eV)}{m_e c^2}} = -0.28619 \ eV$$
 (14.56)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The transition state comprises O--CO, oxygen binding to CO. Vibration of the linear XYZ-molecular transition state corresponds to  $v_3$  [5] with the maximum kinetic energy localized to the nascent C-O bond. In this case, the kinetic energy of the nuclei is the maximum for this bond. Thus,  $\overline{E}_{Kvib}$  is the vibrational energy. The decrease in the energy of the  $CO_2$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (14.56) and  $\overline{E}_{Kvib}$ , the vibrational energy. Using the experimental  $CO_2$   $E_{vib}(v_3)$  of 2349  $cm^{-1}$  (0.29124 eV) [6] for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{osc}(CO_2)$  is

$$\overline{E}_{osc}(CO_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + E_{vib}$$
(14.57)

$$\overline{E}_{osc}(CO_2) = -0.28619 \ eV + 0.29124 \ eV = 0.00505 \ eV$$
 (14.58)

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### TOTAL AND BOND ENERGIES OF THE CARBON DIOXIDE MOLECULE

 $E_{T+osc}(CO_2)$ , the total energy of  $CO_2$  including the Doppler term, is given by the sum of  $E_T(CO_2)$  (Eq. (14.53)) and  $\overline{E}_{osc}(CO_2)$  given by Eq. (14.58):

$$E_{T+osc}(CO_{2}) = \begin{pmatrix} 2(V_{e} + T + V_{m} + V_{p}) + E(ionization; C) \\ + E(ionization; C^{+}) + E(ionization; O) + 2E(ionization; O^{+}) \\ + 2E_{T}(O, 2p) + \overline{E}_{osc}(CO_{2}) \end{pmatrix}$$

$$= \begin{pmatrix} 2E_{T}(C = O, \sigma) + E(ionization; C) + E(ionization; C^{+}) \\ + E(ionization; O) + 2E(ionization; O^{+}) \\ + 2E_{T}(O, 2p) + \overline{E}_{osc}(CO_{2}) \end{pmatrix}$$

$$= E_{T}(CO_{2}) + \overline{E}_{osc}(CO_{2})$$

$$(14.59)$$

$$\begin{cases} 2 \left( \frac{-4e^2}{8\pi\varepsilon_0 \sqrt{\frac{2aa_0}{3}}} \left( \frac{3}{2} \right) \ln \frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1 \right) + E(ionization; C) \\ + E(ionization; C^+) + E(ionization; O) \\ + 2E(ionization; O^+) - 2 \sum_{O,n=4}^{5} \frac{(Z - n)e^2}{8\pi\varepsilon_0} \left( \frac{1}{r_6} - \frac{1}{r_8} \right) \end{cases}$$

$$\begin{cases} \sqrt{\frac{4(0.75)e^2}{4\pi\varepsilon_0 b^3}} \\ 1 + \frac{1}{2} \sqrt{\frac{4\pi\varepsilon_0 b^3}{m_e}} \\ -55.26841 \ eV - 0.28619 \ eV + E_{vib} \end{cases}$$

(14.60)

5

From Eqs. (14.57-14.60), the total energy of the CO<sub>2</sub> MO is

$$E_{T+asc}(CO_2) = -55.25476 \ eV + \overline{E}_{asc}(CO_2)$$

$$= -55.25476 \ eV + 0.00505 \ eV$$

$$= -55.26336 \ eV$$
(14.61)

where the experimental  $E_{vib}$  was used.

As in the case of the dissociation of the bond of the hydroxyl radical, an oxygen atom is formed with dissociation of  $CO_2$ . O has two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is

reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101):

$$E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_0 \mu_B^2}{a_0^3} = 0.11441 \ eV$$
 (14.62)

The  $CO_2$  bond dissociation energy,  $E_D(CO_2)$ , is given by the sum of the energies of the CO 5 and the O atom minus the sum of  $E_{T+osc}(CO_2)$  and E(magnetic):

$$E_D(CO_2) = E(CO) + E(O) - \left(E(magnetic) + E_{T+asc}(CO_2)\right)$$
 (14.63)

The energy of an oxygen atom is given by Eq. (14.14) and  $E_T(CO)$  is given by the sum of the experimental energies of C (Eq. (14.12)), O (Eq. (14.14)), and the negative of the bond energy of CO (Eq. (13.914)):

10 
$$E(CO) = -11.26030 \ eV - 13.618060 \ eV - 11.15696 \ eV = -36.03532 \ eV$$
 (14.64)

The energy of O is given by the negative of the corresponding ionization energy given in Eq. (4.14). Thus, the  $CO_2$  bond dissociation energy,  $E_D(CO_2)$ , given by the Eqs. (4.14) and (14.61-14.64) is

$$E_D(CO_2) = -(36.03532 \ eV + 13.618060 \ eV) - (E(magnetic) + E_{T+osc}(CO_2))$$

$$= -49.65338 \ eV - (0.11441 \ eV - 55.26336 \ eV)$$

$$= 5.49557 \ eV$$
(14.65)

15 The experimental CO<sub>2</sub> bond dissociation energy is [7]

$$E_{D298}(CO_2) = 5.516 \, eV$$
 (14.66)

The results of the determination of bond parameters of  $CO_2$  are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and 20 calculated results is excellent.

#### NITROGEN DIOXIDE MOLECULE

The nitrogen dioxide molecule can be formed by the reaction of nitric oxide and an oxygen atom:

$$NO + O \rightarrow NO_2 \tag{14.67}$$

The bonding in the nitrogen dioxide molecule comprises two double bonds, each a  $H_2$ -type MO with four paired electrons wherein the central N atom is shared by both bonds such that six electrons can be assigned to the two N=O bonds. Thus, two N2p electrons combine

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with the four O2p electrons, two from each O, as a linear combination to form the two overlapping N=O bonds of  $NO_2$ . The force balance equation and radius  $r_7$  of the 2p shell of N is derived in the Seven-Electron Atoms section. The force balance equation and radius  $r_8$  of the 2p shell of O is derived in the Eight-Electron Atoms section. With the formation of each of the two  $H_2$ -type MOs by the contribution of two 2p electrons each from the N and O atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the 2s and 2p electrons of N and O, and the  $H_2$ -type MO. This force from N and O causes the  $H_2$ -type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining N and O electrons decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of  $NO_2$  is  $N1s^2O_11s^2O_21s^2N2s^2O_12s^2O_22s^2N2p^1O_12p^2O_22p^2\sigma_{O_1,N,O_1}^6$  where the subscripts designate the O atom, 1 or 2,  $\sigma$  designates the  $H_2$ -type MO, and the orbital arrangement is

15

Nitrogen dioxide is predicted to be weakly paramagnetic in agreement with observations [1].

# FORCE BALANCE OF THE 2p SHELL OF THE NITROGEN ATOM OF NITROGEN DIOXIDE

For the N atom, force balance for the outermost 2p electron of  $NO_2$  (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to 5 interactions between electron 5 and the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most 2p shell electron of NO (electron 5) due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_s^2} \mathbf{i_r} \tag{14.69}$$

10 for  $r > r_4$ . The 2p shell possess a +2 external electric field given by Eq. (10.92) for  $r > r_5$ . The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of N in  $NO_2$  are the same as those of N in NO. They are also the same as those of N in the nitrogen molecule with  $r_5$  replacing  $r_6$  and with an increase of the central field by an integer. The diamagnetic force,  $\mathbf{F}_{diamagnetic}$ , of Eq. (10.82) due to the p15 orbital contribution is given by Eq. (13.918):

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right) \frac{\hbar^2}{4m_e r_s^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{\hbar^2}{12m_e r_s^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r$$
 (14.70)

And,  $F_{mag 2}$  corresponding to the conserved orbital angular momentum of the three orbitals is also the same as that of  $NO_2$  given by Eq. (13.919):

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{3\hbar^2}{m_e r_s^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
 (14.71)

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_5$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is given by Eq. (13.920):

$$\mathbf{F}_{diamognetic\ 2} = -\left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_s^4} 10\sqrt{s(s+1)} \mathbf{i}_r$$
 (14.72)

The radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (14.69)) and diamagnetic (Eqs. (14.70) and (14.72)), and paramagnetic (Eq. (14.71)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \begin{pmatrix}
\frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \frac{\hbar^2}{12m_e r_5^2 r_3} \sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_5^2 r_3} \sqrt{s(s+1)} \\
- \left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_5^4 m_e} 10\sqrt{s(s+1)}$$
(14.73)

Substitution of  $v_5 = \frac{\hbar}{m_e r_5}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (14.73) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \frac{\hbar^2}{12m_e r_5^2 r_3} \sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_5^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_5^4 m_e} 10\sqrt{\frac{3}{4}}$$
(14.74)

The quadratic equation corresponding to Eq. (14.74) is

$$r_{5}^{2} - \frac{\frac{\hbar^{2}}{m_{e}}}{\left(\frac{(Z-4)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} r_{5} - \frac{\frac{\hbar^{2}}{m_{e}}\left[\frac{Z-5}{Z-4}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_{3}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-4)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} = 0$$

$$(14.75)$$

The solution of Eq. (14.75) using the quadratic formula is:

$$r_{5} = \frac{a_{0}}{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{2}} + \frac{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{2}}{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

$$(14.76)$$

r<sub>3</sub> in units of a<sub>0</sub>

The positive root of Eq. (14.76) must be taken in order that  $r_5 > 0$ . Substitution of  $\frac{r_3}{a_0} = 0.69385$  (Eq. (10.62) with Z = 7) into Eq. (14.76) gives

$$r_{\rm s} = 0.74841a_0 \tag{14.77}$$

## FORCE BALANCE OF THE 2p SHELL OF EACH OXYGEN ATOM OF NITROGEN DIOXIDE

15 For each O atom, force balance for the outermost 2p electron of  $NO_2$  (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due

to interactions between electron 6 and the other 2p electron as well as the 2s-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most 2p shell electron of  $NO_2$  (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} \mathbf{i}_r \tag{14.78}$$

for  $r > r_5$ . The 2p shell possess an external electric field of +2 given by Eq. (10.92) for  $r > r_6$ . The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of O in  $NO_2$  are the same as those of O in NO. The diamagnetic force,  $F_{diamagnetic}$ , of Eq. (10.82) due to the p-orbital contribution given by Eq. (13.927) is

$$\mathbf{F}_{diamognetic} = -\left(\frac{2}{3}\right) \frac{\hbar^2}{4m_e r_e^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_e^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r$$
 (14.79)

And,  $F_{mag 2}$  corresponding to the conserved spin and orbital angular momentum given by Eq. (13.928) is

15 
$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{2\hbar^2}{m_e r_b^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
 (14.80)

The electric field external to the 2p shell given by Eq. (10.92) for  $r > r_6$  gives rise to a second diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , given by Eq. (10.93).  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +2 outside of its radius given by Eq. (13.929) is

20 
$$\mathbf{F}_{diamagnetic 2} = -\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_6^4} 10 \sqrt{s(s+1)} \mathbf{i_r}$$
 (14.81)

In addition, the contribution of two 2p electrons in the formation of the  $\sigma$  MO gives rise to a paramagnetic force on the remaining paired 2p electrons. The force  $\mathbf{F}_{mog 3}$  is given by Eq. (13.930) is

$$\mathbf{F}_{mag \ 3} = \frac{\hbar^2}{4m_s r_s^3} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}}$$
 (14.82)

The radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (14.78)) and diamagnetic (Eqs. (14.79) and (14.81)), and

paramagnetic (Eqs. (14.80) and (14.82)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \begin{cases}
\frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3} \sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3} \sqrt{s(s+1)} \\
-\left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_6^4 m_e} 10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3} \sqrt{s(s+1)}
\end{cases}$$
(14.83)

Substitution of  $v_6 = \frac{\hbar}{m_e r_6}$  (Eq. (1.56)) and  $s = \frac{1}{2}$  into Eq. (14.83) gives:

$$\frac{\hbar^{2}}{m_{e}r_{6}^{3}} - \frac{\hbar^{2}}{4m_{e}r_{6}^{3}} \sqrt{\frac{3}{4}} = \frac{(Z-5)e^{2}}{4\pi\varepsilon_{0}r_{6}^{2}} - \frac{2\hbar^{2}}{12m_{e}r_{6}^{2}r_{3}} \sqrt{\frac{3}{4}} + \frac{2\hbar^{2}}{Zm_{e}r_{6}^{2}r_{3}} \sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_{3}\hbar^{2}}{r_{6}^{4}m_{e}} 10\sqrt{\frac{3}{4}}$$

$$(14.84)$$

The quadratic equation corresponding to Eq. (14.84) is

$$r_{6}^{2} - \frac{\frac{\hbar^{2}}{m_{e}} \left(1 - \frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z - 5)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{2}{12} - \frac{2}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} r_{6} - \frac{\frac{\hbar^{2}}{m_{e}} \left[\frac{Z - 6}{Z - 5}\right] \left(1 - \frac{\sqrt{2}}{2}\right)r_{3}10\sqrt{\frac{3}{4}}}{\left(\frac{(Z - 5)e^{2}}{4\pi\varepsilon_{0}} - \left(\frac{2}{12} - \frac{2}{Z}\right)\frac{\hbar^{2}}{m_{e}r_{3}}\sqrt{\frac{3}{4}}\right)} = 0$$
(14.85)

The solution of Eq. (14.85) using the quadratic formula is:

$$a_{0}\left(1-\frac{\sqrt{3}}{8}\right) = \left(\frac{1-\frac{\sqrt{3}}{8}}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{2}} + \frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

$$r_{6} = \frac{20\sqrt{3}\left(\frac{Z-6}{Z-5}\right)\left(1-\frac{\sqrt{2}}{2}\right)r_{3}}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

$$r_{6} = \frac{20\sqrt{3}\left(\frac{Z-6}{Z-5}\right)\left(1-\frac{\sqrt{2}}{2}\right)r_{3}}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

 $r_{3}$  in units of  $a_{0}$ 

The positive root of Eq. (14.86) must be taken in order that  $r_6 > 0$ . Substitution of  $\frac{r_3}{a_0} = 0.59020$  (Eq. (10.62) with Z = 8) into Eq. (14.86) gives

$$r_{s} = 0.70460a_{0} \tag{14.87}$$

15 ENERGIES OF THE 2p SHELLS OF THE NITROGEN ATOM AND

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### OXYGEN ATOMS OF NITROGEN DIOXIDE

Consider the determination of the total energy of  $NO_2$  from the reaction of a nitrogen atom with two oxygen atoms. With the formation of each  $H_2$ -type MO by the contribution of two 2p electrons from each of the N and the two O atoms, the total energy of the  $NO_2$  molecule, which is subtracted from the sum of the energies of the nitrogen and oxygen atoms to determine the bond energy, is increased by the ionization energies of N,  $N^+$ , O, and  $2O^+$  given by Eqs. (14.88-14.91), respectively. Experimentally, the energies are [2]

$$E(ionization; N) = 14.53414 \, eV$$
 (14.88)

$$E(ionization; N^+) = 29.6013 \ eV$$
 (14.89)

10 
$$E(ionization; O) = 13.61806 eV$$
 (14.90)

$$E(ionization; O^{+}) = 35.11730 \, eV$$
 (14.91)

In addition, the central forces on the 2p shells of the N and O atoms are increased with the formation of the  $\sigma$  MOs which reduces each shell's radius and increases its total energy. The change per bond is the same as that of NO since the final radii given by Eq. 15 (14.77) and (14.87) are the same for NO and  $NO_2$ . The Coulombic energy terms of the total energy of the N and O atoms at the new radii are calculated and added to the ionization energies of N,  $N^+$ , O, and  $2O^+$ , and the energy of the  $\sigma$  MOs to give the total energy of  $NO_2$ . Then, the bond energy is determined from the total  $NO_2$  energy.

The radius  $r_7$  of the nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084a_0 \tag{14.92}$$

Using the initial radius  $r_7$  of the N atom and the final radius  $r_5$  of the N2p shell (Eq. (14.77)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(N,2p)$  of the Coulombic energy change of the N2p electrons of the N atom is determined using Eq. (10.102):

$$E_{T}(N,2p) = -\sum_{n=4}^{4} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{5}} - \frac{1}{r_{7}}\right)$$

$$= -(13.60580 \ eV)(0.26186)(3)$$

$$= -10.68853 \ eV$$
(14.93)

The radius  $r_8$  of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 ag{14.94}$$

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Using the initial radius  $r_8$  of the O atom and the final radius  $r_6$  of the O2p shell (Eq. (14.87)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum  $E_T(O,2p)$  of the Coulombic energy change of the O2p electrons of the O atom is determined using Eq. (10.102):

$$E_T(O,2p) = \sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_6} - \frac{1}{r_8}\right)$$

$$= (13.60580 \ eV)(0.41925a_0^{-1})(3+4)$$

$$= -39.92918 \ eV$$
(14.95)

#### FORCE BALANCE OF THE $\sigma$ MO OF NITROGEN DIOXIDE

5

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having +2e at each focus and a first bound pair. Then, the forces are the same 10 as those of a molecule ion having +e at each focus. The diamagnetic force  $\mathbf{F}_{diamagneticMO1}$  for each  $\sigma$ -MO of the  $NO_2$  molecule due to the two paired electrons in the O2p shell is given by Eq. (13.633) with  $n_e = 2$ :

$$\mathbf{F}_{diamagneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$
 (14.96)

This is also the corresponding force of NO given by Eq. (13.942).  $\mathbf{F}_{diamagneticMO2}$  of the 15 nitrogen dioxide molecule comprising nitrogen with charge  $Z_1 = 7$  and  $|L_1| = \hbar$  and  $|L_2| = \sqrt{\frac{3}{4}}\hbar$  and the two oxygen atoms, each with  $Z_2 = 8$  and  $|L_3| = \hbar$  is given by the corresponding sum of the contributions. Using Eq. (13.835),  $\mathbf{F}_{diamagneticMO2}$  for  $NO_2$  is

$$\mathbf{F}_{diamogneticMO2} = \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$
 (14.97)

This is also the corresponding force of NO given by Eq. (13.943) except the term due to oxygen is twice that of NO due to the two oxygen atoms of  $NO_2$ . The general force balance equation for the  $\sigma$ -MO of the nitrogen dioxide molecule given by Eqs. (11.200), and (14.97-14.98) is also the same as that of CN (Eq. (14.836)) except for the doubling of the  $\frac{2}{Z_2}$  term due to the two oxygen atoms:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$
 (14.98)

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D - \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$
 (14.99)

$$\left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D$$
(14.100)

$$a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) a_0 \tag{14.101}$$

5 Substitution of  $Z_1 = 7$  and  $Z_2 = 8$  into Eq. (14.101) gives

$$a = 2.51658a_0 = 1.33171 \ X \ 10^{-10} \ m \tag{14.102}$$

Substitution of Eq. (14.102) into Eq. (11.79) is

$$c' = 1.12173a_0 = 5.93596 \ X \ 10^{-11} \ m \tag{14.103}$$

The internuclear distance given by multiplying Eq. (14.103) by two is

$$2c' = 2.24347a_0 = 1.18719 X 10^{-10} m ag{14.104}$$

The experimental bond distance is [3]

$$2c' = 1.193 X \cdot 10^{-10} m \tag{14.105}$$

Substitution of Eqs. (14.102-14.103) into Eq. (11.80) is

$$b = c = 2.25275a_0 = 1.19210 \ X \ 10^{-10} \ m \tag{14.106}$$

15 Substitution of Eqs. (14.102-14.103) into Eq. (11.67) is

$$e = 0.44574 \tag{14.107}$$

The bonding in the nitrogen dioxide molecule comprises two double bonds, each a  $H_2$ -type MO with four paired electrons wherein the central N atom is shared by both bonds such that six electrons can be assigned to the two N=O bonds. Thus, two N2p electrons combine with the four O2p electrons, two from each O, as a linear combination to form the two overlapping N=O bonds of  $NO_2$ . Using the electron configuration of  $NO_2$  (Eq.

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(14.68)), the radii of the  $N1s = 0.14605a_0$  (Eq. (10.51)),  $N2s = 0.69385a_0$  (Eq. (10.62)),  $N2p = 0.74841a_0$  (Eq. (14.77)),  $O1s = 0.12739a_0$  (Eq. (10.51)),  $O2s = 0.59020a_0$  (Eq. (10.62)), and  $O2p = 0.70460a_0$  (Eq. (14.87)) shells and the parameters of the  $\sigma$  MOs of  $NO_2$  given by Eqs. (13.3-13.4), (14.102-14.104), and (14.106-14.107), the dimensional 5 diagram and charge-density of the  $NO_2$  MO are shown in Figures 35 and 36, respectively.

### SUM OF THE ENERGIES OF THE $\sigma$ MOs AND THE AOs OF NITROGEN DIOXIDE

The energies of each  $NO_2$   $\sigma$  MO are the same as those of NO (Eqs. (13.954-13.958)). They are given by the substitution of the semiprincipal axes (Eqs. (14.102-14.103) and (14.106)) into the energy equations (Eqs. (11.207-11.212)) of  $H_2$  except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the  $\sigma$ -MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -93.03032 \ eV$$
 (14.108)

15 
$$V_p = 2^2 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 48.51704 \ eV$$
 (14.109)

$$T = 2\frac{\hbar^2}{2m \, a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 9.24176 \, eV \tag{14.110}$$

$$V_{m} = 2^{2} \frac{-\hbar^{2}}{4m_{c}a\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} = -9.24176 \, eV$$
 (14.111)

$$E_T = V_e + T + V_m + V_p (14.112)$$

Substitution of Eqs. (11.79) and (14.108-14.111) into Eq. (14.112) gives

20 
$$E_{T}(N=O,\sigma) = \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left(8\ln\frac{a+\sqrt{\frac{aa_{0}}{2}}}{a-\sqrt{\frac{aa_{0}}{2}}}-4\right) = -44.51329 \, eV$$
 (14.113)

where  $E_T(N=O,\sigma)$  is the total energy of each  $\sigma$  MO of  $NO_2$ . The total energy of  $NO_2$ ,  $E_T(NO_2)$ , is given by the sum of E(ionization; N) and  $E(ionization; N^+)$ , the sum of the energies of the first and second electrons of nitrogen (Eqs. (14.88-14.89)) donated to each

double bond, the sum of E(ionization; O) and two times  $E(ionization; O^{+})$ , the energies of the first and second electrons of oxygen (Eqs. (14.90-14.91)) donated to the double bonds,  $E_{\tau}(N,2p)$ , the N2p AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.93)), two times  $E_T(0,2p)$ , the O2p AO contribution due to the 5 decrease in radius with the formation of each bond (Eq. (14.95)), and two times  $E_T(N=0,\sigma)$ , the  $\sigma$  MO contribution given by Eq. (14.113):

$$E_{T}(NO_{2}) = \begin{cases} E(ionization; N) + E(ionization; N^{+}) \\ + E(ionization; O) + 2E(ionization; O^{+}) + E_{T}(N, 2p) \\ + 2E_{T}(O, 2p) + 2E_{T}(N = O, \sigma) \end{cases}$$

$$= \begin{pmatrix} 14.53414 \ eV + 29.6013 \ eV + 13.61806 \ eV \\ + 2(35.11730 \ eV) + (-10.68853) + 2(-39.92918 \ eV) \\ + 2\left(\frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}} \left(8\ln\frac{a + \sqrt{\frac{aa_{0}}{2}}}{a - \sqrt{\frac{aa_{0}}{2}}} - 4\right)\right) \\ = \begin{pmatrix} 14.53414 \ eV + 29.6013 \ eV + 13.61806 \ eV \\ + 2(35.11730 \ eV) + (-10.68853) \\ + 2(-39.92918 \ eV) + 2(-44.51329 \ eV) \end{pmatrix}$$

$$= -51.58536 \ eV$$

#### VIBRATION OF NO,

10 The vibrational energy levels of NO<sub>2</sub> may be solved by determining the Morse potential curve from the energy relationships for the transition from a N atom and two O atoms whose parameters are given by Eqs. (10.134-10.143) and (10.154-10.163), respectively, to a N atom whose parameter  $r_5$  is given by Eq. (14.77), two O atoms whose parameter  $r_6$  is given by Eq. (14.87), and the  $\sigma$  MOs whose parameters are given by Eqs. (14.102-14.104) 15 and (14.106.-14.107). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [4] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by 20 perturbation methods.

#### THE DOPPLER ENERGY TERMS OF NITROGEN DIOXIDE

The equations of the radiation reaction force of nitrogen dioxide are the same as those of NO with the substitution of the  $NO_2$  parameters. Using Eq. (13.961), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{4e^2}{4\pi\varepsilon_0 a^3}} = 2.07110 \, X \, 10^{16} \, rad/s \tag{14.115}$$

where a is given by Eq. (14.102). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_{K} = \hbar \omega = \hbar 2.07110 \, X \, 10^{16} \, rad/s = 13.63231 \, eV$$
 (14.116)

10 In Eq. (11.181), substitution of  $E_T(NO_2)/2$  for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.116) for  $\overline{E}_K$  gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{hv} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -25.79268 \ eV \sqrt{\frac{2e(13.63231 \ eV)}{m_e c^2}} = -0.18840 \ eV$$
 (14.117)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The transition state comprises O--NO, oxygen binding to NO. As in the case of  $CO_2$  bond formation, vibration in the transition state corresponds to  $v_3$  [5] with the maximum kinetic energy localized to the nascent N-O bond. In this case, the kinetic energy of the nuclei is the maximum for this bond. Thus,  $\overline{E}_{Kvib}$  is the vibrational energy. The decrease in the energy of the  $NO_2$  MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (14.117) and  $\overline{E}_{Kvib}$ , the vibrational energy. Using the experimental  $NO_2$   $E_{vib}(v_3)$  of  $1618 \ cm^{-1}$  (0.20061 eV) [6] for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{osc}(NO_2)$  is

$$\overline{E}_{osc}(NO_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + E_{vib}$$
(14.118)

25 
$$\overline{E}_{\alpha c}(NO_2) = -0.18840 \ eV + 0.20061 \ eV = 0.01221 \ eV$$
 (14.119)

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#### TOTAL AND BOND ENERGIES OF NITROGEN DIOXIDE

 $E_{T+ass}(NO_2)$ , the total energy of  $NO_2$  including the Doppler term, is given by the sum of  $E_T(NO_2)$  (Eq. (14.114)) and  $\overline{E}_{osc}(NO_2)$  given by Eq. (14.119):

$$E_{T+osc}(NO_{2}) = \begin{cases} 2(V_{e} + T + V_{m} + V_{p}) + E(ionization; N) + E(ionization; N^{+}) \\ + E(ionization; O) + 2E(ionization; O^{+}) \\ + E_{T}(N, 2p) + 2E_{T}(O, 2p) + \overline{E}_{osc}(NO_{2}) \end{cases}$$

$$= \begin{cases} 2E_{T}(N = O, \sigma) + E(ionization; N) + E(ionization; N^{+}) \\ + E(ionization; O) + 2E(ionization; O^{+}) \\ + E_{T}(N, 2p) + 2E_{T}(O, 2p) + \overline{E}_{osc}(NO_{2}) \end{cases}$$

$$= E_{T}(NO_{2}) + \overline{E}_{osc}(NO_{2})$$

$$(14.120)$$

$$E_{T+osc}(NO_{2}) = \begin{cases} 2\left(\frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2}}}\left(8\ln\frac{a+\sqrt{\frac{aa_{0}}{2}}}{a-\sqrt{\frac{aa_{0}}{2}}}-4\right)\right) \\ E(ionization; N) + E(ionization; N^{+}) \\ + E(ionization; O) + 2E(ionization; O^{+}) \\ -\sum_{N,n=4}^{4} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}}\left(\frac{1}{r_{5}}-\frac{1}{r_{7}}\right) - 2\sum_{O,n=4}^{5} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0}}\left(\frac{1}{r_{6}}-\frac{1}{r_{8}}\right) \end{cases} \\ \left(14.121\right) \\ \left(\frac{1}{1+\frac{1}{2}}\sqrt{\frac{4e^{2}}{4\pi\varepsilon_{o}a^{3}}} + E_{vib}\right) \\ = -51.58536 \ eV - 0.18840 \ eV + E_{vib} \end{cases}$$

From Eqs. (14.119-14.121), the total energy of the  $NO_2$  MO is

$$E_{T+osc}(NO_2) = -51.58536 \ eV + \overline{E}_{osc}(NO_2)$$

$$= -51.58536 \ eV + 0.01221 \ eV$$

$$= -51.57315 \ eV$$
(14.122)

where the experimental  $E_{vib}$  was used.

5

As in the case of the dissociation of the bond of the hydroxyl radical, an oxygen atom 10 is formed with dissociation of  $NO_2$ . O has two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is

reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101):

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_o \mu_B^2}{a_0^3} = 0.11441 \ eV$$
 (14.123)

The  $NO_2$  bond dissociation energy,  $E_D(NO_2)$ , is given by the sum of the energies of the 5 NO and the O atom minus the sum of  $E_{T+osc}(NO_2)$  and E(magnetic):

$$E_D(NO_2) = E(NO) + E(O) - (E(magnetic) + E_{T+osc}(NO_2))$$
(14.124)

The energy of an oxygen atom is given by the negative of Eq. (14.90), and  $E_T(NO)$  is given by the sum of the experimental energies of N (negative of Eq. (14.88)), O, and the negative of the bond energy of NO (Eq. (13.974)):

10 
$$E(NO) = -14.53414 \, eV - 13.618060 \, eV - 6.53529 \, eV = -34.68749 \, eV$$
 (14.125)

Thus, the  $NO_2$  bond dissociation energy,  $E_D(NO_2)$ , given by Eqs. (4.90) and (14.112-14.125) is

$$E_D(NO_2) = -(34.68749 \ eV + 13.618060 \ eV) - (E(magnetic) + E_{T+osc}(NO_2))$$

$$= -48.30555 \ eV - (0.11441 \ eV - 51.57315 \ eV)$$

$$= 3.15319 \ eV$$
(14.126)

The experimental  $NO_2$  bond dissociation energy is [7]

15 
$$E_{D298}(NO_2) = 3.161 \, eV$$
 (14.127)

## BOND ANGLE OF NO.

The  $NO_2$  MO comprises a linear combination of two N=O-bond MOs. A bond is also possible between the two O atoms of the N=O bonds. Such O=O bonding would 20 decrease the N=O bond strength since electron density would be shifted from the N=O bonds to the O=O bond. Thus, the bond angle between the two N=O bonds is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal O atoms of the N=O bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the O=O ellipsoidal MO is

25 
$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}}$$
 (14.128)

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.129}$$

The length of the semiminor axis of the prolate spheroidal O = O MO b = c is given by Eq. (13.167).

The component energies and the total energy  $E_T$  of the O=O bond are given by the 5 energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of  $H_2$  except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the O=O double bond with two pairs of paired electrons. Substitution of Eq. (14.128) into Eqs. (11.207-11.212) gives

$$0 = \begin{bmatrix} \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left( 8\ln\frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 4 \right) \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{4e^2}{4\pi\varepsilon_0a^3}}}{\frac{m_e}{m_e}c^2}} \right] \\ + \frac{1}{2}\hbar\sqrt{\frac{\frac{4e^2}{8\pi\varepsilon_0a^3} - \frac{4e^2}{8\pi\varepsilon_0(a + c')^3}}{8m_p}}$$
(14.130)

10 From the energy relationship given by Eq. (14.130) and the relationship between the axes given by Eqs. (14.128-14.129) and (13.167-14.168), the dimensions of the O = O MO can be solved.

The most convenient way to solve Eq. (14.130) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 8.3360a_0 = 4.4112 X 10^{-10} m ag{14.131}$$

Substitution of Eq. (14.131) into Eq. (14.128) gives

$$c' = 2.0416a_0 = 1.0804 \ X \ 10^{-10} \ m \tag{14.132}$$

The internuclear distance given by multiplying Eq. (14.132) by two is

$$2c' = 4.0831a_0 = 2.1607 X 10^{-10} m ag{14.133}$$

20 Substitution of Eqs. (14.131-14.132) into Eq. (14.167) gives

$$b = c = 8.0821a_0 = 4.2769 \ X \ 10^{-10} \ m \tag{14.134}$$

Substitution of Eqs. (14.131-14.132) into Eq. (14.168) gives

$$e = 0.2449 \tag{14.135}$$

From,  $2c'_{c=c}$  (Eq. (14.133)), the distance between the two O atoms when the total 25 energy of the corresponding MO is zero (Eq. (14.130)), and  $2c'_{N=O}$  (Eq. (14.104)), the

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internuclear distance of each N=O bond, the corresponding bond angle can be determined from the law of cosines. Using, Eqs. (13.240-13.242), the bond angle  $\theta$  between the N=O bonds is

$$\theta = \cos^{-1} \left( \frac{2(2.24347)^2 - (4.0831)^2}{2(2.24347)^2} \right)$$

$$= \cos^{-1} (-0.6562)$$

$$= 131.012^{\circ}$$
(14.136)

5 The experimental angle between the N = O bonds is [3]

$$\theta = 134.1^{\circ}$$
 (14.137)

The results of the determination of bond parameters of  $NO_2$  are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and 10 calculated results is excellent.

#### ETHANE MOLECULE (CH<sub>3</sub>CH<sub>3</sub>)

The ethane molecule  $CH_3CH_3$  is formed by the reaction of two methyl radicals:

$$CH_3 + CH_3 \rightarrow CH_3CH_3 \tag{14.138}$$

15 CH<sub>3</sub>CH<sub>3</sub> can be solved using the same principles as those used to solve CH<sub>3</sub>, wherein the 2s and 2p shells of each C hybridize to form a single 2sp³ shell as an energy minimum, and the sharing of electrons between two C2sp³ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of three H atomic orbitals (AOs) combine with two sets of three carbon 2sp³ HOs to form two methyl groups comprising a linear combination of six diatomic H<sub>2</sub>-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two CH<sub>3</sub> groups bond by forming a H<sub>2</sub>-type MO between the remaining C2sp³ HO on each carbon.

#### 25 FORCE BALANCE OF THE C-C-BOND MO OF ETHANE

 $CH_3CH_3$  comprises a chemical bond between two  $CH_3$  radicals wherein each methyl radical comprises three chemical bonds between carbon and hydrogen atoms. The solution of the parameters of  $CH_3$  is given in the Methyl Radical  $(CH_3)$  section. Each C-H bond of

CH<sub>3</sub> having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% H<sub>2</sub>-type ellipsoidal MO and 25% C2sp³ HO. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of H<sub>2</sub>, each of the three C-H-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into C2sp³ HO for distances shorter than the radius of the C2sp³ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the C2sp³ shell at the C atom whose nucleus serves as the other focus. The electron configuration and the energy, E(C,2sp³), of the C2sp³ shell is 10 given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each C-H bond is provided by the spin-pairing force of the CH<sub>3</sub> MO that has the symmetry of an s orbital that superimposes with the C2sp³ orbitals such that the corresponding angular momenta are unchanged.

Two  $CH_3$  radicals bond to form  $CH_3CH_3$  by forming a MO between the two 15 remaining  $C2sp^3$ -HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between two  $C2sp^3$  HOs to form a molecular orbital (MO) comprising two spin-paired electrons permits each  $C2sp^3$  HO to decrease in radius and energy.

As in the case of the C-H bonds, the C-C-bond MO is a prolate-spheroidal-MO surface that cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  20 shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the  $C2sp^3$  shell at each C atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  shell. As in the case of previous examples of energy-matched MOs such as those of OH, NH, CH, and the C=O-bond MO of  $CO_2$ , the C-C-bond MO of ethane must comprise 75% of a  $H_2$ -type ellipsoidal MO 25 in order to match potential, kinetic, and orbital energy relationships. Thus, the C-C-bond MO must comprise two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the two  $C2sp^3$  HOs:

The linear combination of the  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution from each  $C2sp^3$  HO to the C-C-bond MO to achieve an energy minimum. The force balance of the C-C-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.139) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

Similarly, the energies of each  $CH_3$  MO involve each  $C2sp^3$  and each H1s electron with the formation of each C-H bond. The sum of the energies of the  $H_2$ -type ellipsoidal 10 MOs is matched to that of the  $C2sp^3$  shell. This energy is determined by the considering the effect of the donation of 25% electron density from the two  $C2sp^3$  HOs to the C-C-bond MO. The  $2sp^3$  hybridized orbital arrangement given by Eq. (13.422) is

15

where the quantum numbers  $(\ell, m_{\ell})$  are below each electron. The total energy of the state is given by the sum over the four electrons. The sum  $E_T(C,2sp^3)$  of calculated energies of C,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is  $E_T(C,2sp^3) = 64.3921 \ eV + 48.3125 \ eV + 24.2762 \ eV + 11.27671 \ eV$   $= 148.25751 \ eV$ 

which agrees well with the sum of  $148.02532 \, eV$  from the experimental [2] values. Consider the case of the  $C2sp^3$  HO of each methyl radical. The orbital-angular-momentum interactions cancel such that the energy of the  $E_T(C,2sp^3)$  is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{2sp^3}$  of the  $C2sp^3$  shell may be calculated from the Coulombic energy using 25 Eq. (10.102):

$$r_{2sp^3} = \sum_{n=2}^{5} \frac{(Z - n)e^2}{8\pi\varepsilon_0 \left(e148.25751 \, eV\right)} = \frac{10e^2}{8\pi\varepsilon_0 \left(e148.25751 \, eV\right)} = 0.91771a_0 \tag{14.142}$$

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where Z=6 for carbon. Using Eqs. (10.102) and (14.142), the Coulombic energy  $E_{Coulomb}(C,2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E_{Coulomb}\left(C, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.91771a_{0}} = -14.82575 \ eV \tag{14.143}$$

During hybridization, one of the spin-paired 2s electrons is promoted to  $C2sp^3$  shell as an 5 unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152) at the initial radius of the 2s electrons. From Eq. (10.62) with Z=6, the radius  $r_3$  of C2s shell is

$$r_3 = 0.84317a_0 \tag{14.144}$$

Using Eqs. (13.152) and (14.144), the unpairing energy is

10 
$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.84317a_0)^3} = 0.19086 \ eV$$
 (14.145)

Using Eqs. (14.143) and (14.145), the energy  $E(C, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E(C,2sp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(r_{3})^{3}}$$

$$= -14.82575 \ eV + 0.19086 \ eV$$

$$= -14.63489 \ eV$$
(14.146)

Next, consider the formation of the C-C-bond MO of ethane from two methyl radicals, each having a  $C2sp^3$  electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum  $E_T(C_{ethane}, 2sp^3)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$E_T(C_{ethane}, 2sp^3) = -(64.3921 eV + 48.3125 eV + 24.2762 eV + E(C, 2sp^3))$$

$$= -(64.3921 eV + 48.3125 eV + 24.2762 eV + 14.63489 eV)(14.147)$$

$$= -151.61569 eV$$

20 where  $E(C,2sp^3)$  is the sum of the energy of C,  $-11.27671\,eV$ , and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the  $E_T(C_{ethane},2sp^3)$  is purely Coulombic.

The sharing of electrons between two  $C2sp^3$  HOs to form a C-C-bond MO permits

each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each  $C2sp^3$  HO donates an excess of 25% of its electron density to the C-C-bond MO to form an energy minimum. By considering this electron redistribution in the ethane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{ethane2sp^3}$  of the  $C2sp^3$  shell of ethane may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{ethane 2 sp^{3}} = \left(\sum_{n=2}^{5} (Z - n) - 0.25\right) \frac{e^{2}}{8\pi\varepsilon_{0} \left(e151.61569 \, eV\right)}$$

$$= \frac{9.75e^{2}}{8\pi\varepsilon_{0} \left(e151.61569 \, eV\right)}$$

$$= 0.87495a_{0}$$
(14.148)

Using Eqs. (10.102) and (14.148), the Coulombic energy  $E_{Coulomb}\left(C_{ethane}, 2sp^3\right)$  of the outer 10 electron of the  $C2sp^3$  shell is

$$E_{Coulomb} \left( C_{ethane}, 2sp^{3} \right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{ethane2sp^{3}}}$$

$$= \frac{-e^{2}}{8\pi\varepsilon_{0}0.87495a_{0}}$$

$$= -15.55033 eV$$
(14.149)

During hybridization, one of the spin-paired 2s electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.149), the energy  $E(C_{ethane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E(C_{ethane}, 2sp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{ethane2sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(r_{3})^{3}}$$

$$= -15.55033 \ eV + 0.19086 \ eV$$

$$= -15.35946 \ eV$$
(14.150)

Thus,  $E_T(C-C,2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of the C-C-bond MO is given by the difference between Eq. (14.146) and Eq. (14.150):

$$E_T(C-C,2sp^3) = E(C_{ethane},2sp^3) - E(C,2sp^3)$$

$$= -15.35946 \ eV - (-14.63489 \ eV)$$

$$= -0.72457 \ eV$$
(14.151)

The  $H_2$ -type ellipsoidal MO comprises 75% of the C-C-bond MO shared between two  $C2sp^3$  HOs corresponding to the electron charge density in Eq. (11.65) of  $\frac{-0.75e}{2}$ . But, the additional 25% charge-density contribution to the C-C-bond MO causes the electron charge density in Eq. (11.65) to be is given by  $\frac{-e}{2} = -0.5e$ . Thus, the force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci given by Eq. (11.65) is

$$k' = \frac{(0.5)2e^2}{4\pi\varepsilon_0} \tag{14.152}$$

The distance from the origin to each focus c' is given by substitution of Eq. (14.152) into Eq. (13.60). Thus, the distance from the origin of the C-C-bond MO to each focus c' is given by

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 a}} = \sqrt{aa_0} \tag{14.153}$$

The internuclear distance from Eq. (14.153) is

$$2c' = 2\sqrt{aa_0} {14.154}$$

The length of the semiminor axis of the prolate spheroidal C-C-bond MO b=c is given by

- Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the C-C-bond MO. Since the C-C-bond MO comprises a H<sub>2</sub>-type-ellipsoidal MO that transitions to the C<sub>ethane</sub> 2sp³ HO of each carbon, the energy E(C<sub>ethane</sub>, 2sp³) in Eq. (14.150) adds to that of the H<sub>2</sub>-type ellipsoidal MO to give the total energy of the C-C-bond MO.
  From the energy equation and the relationship between the axes, the dimensions of the C-C-bond MO are solved. Similarly, E(C<sub>ethane</sub>, 2sp³) is added to the energy of the H<sub>2</sub>-type ellipsoidal MO of each C-H bond of the methyl groups to give its total energy. From the energy equation and the relationship between the axes, the dimensions of the equivalent C-H-bond MOs of the methyl groups in ethane are solved.
- The general equations for the energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of the C-C-bond MO are the same as those of the CH MO as well as each C-H-bond MO of the methyl groups except that energy of the  $C_{ethane}2sp^3$  HO is used. Since the prolate

spheroidal  $H_2$ -type MO transitions to the  $C_{ethane}2sp^3$  HO of each carbon and the energy of the  $C_{ethane}2sp^3$  shell must remain constant and equal to the  $E\left(C_{ethane},2sp^3\right)$  given by Eq. (14.150), the total energy  $E_T\left(C-C,\sigma\right)$  of the  $\sigma$  component of the C-C-bond MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C_{ethane}2sp^3$  HO and the  $H_2$ -type ellipsoidal MO that forms the  $\sigma$  component of the C-C-bond MO as given by Eq. (14.139) with the electron charge redistribution. Using Eqs. (13.431) and (14.150),  $E_T\left(C-C,\sigma\right)$  is given by

$$E_{T}(C-C,\sigma) = E_{T} + E(C_{ethane}, 2sp^{3})$$

$$= -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \ eV$$
(14.155)

To match the boundary condition that the total energy of the entire the  $H_2$ -type ellipsoidal 10 MO is given by Eqs. (11.212) and (13.75),  $E_T(C-C,\sigma)$  given by Eq. (14.155) is set equal to Eq. (13.75):

$$E_{T}(C-C,\sigma) = -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \ eV$$

$$= -31.63536831 \ eV$$
(14.156)

From the energy relationship given by Eq. (14.156) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the C-C-bond MO can 15 be solved.

Substitution of Eq. (14.153) into Eq. (14.156) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{aa_0}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{aa_0}}{a - \sqrt{aa_0}} - 1 \right] = e16.27589$$
 (14.157)

The most convenient way to solve Eq. (14.157) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 2.10725a_0 = 1.11511 \ X \ 10^{-10} \ m \tag{14.158}$$

Substitution of Eq. (14.158) into Eq. (14.153) gives

$$c' = 1.45164a_0 = 7.68173 \ X \ 10^{-11} \ m \tag{14.159}$$

The internuclear distance given by multiplying Eq. (14.159) by two is

$$2c' = 2.90327a_0 = 1.53635 X 10^{-10} m ag{14.160}$$

25 The experimental bond distance is [3]

$$2c' = 1.5351 \ X \ 10^{-10} \ m \tag{14.161}$$

Substitution of Eqs. (14.158-14.159) into Eq. (13.62) gives

$$b = c = 1.52750a_0 = 8.08317 \ X \ 10^{-11} \ m \tag{14.162}$$

Substitution of Eqs. (14.158-14.159) into Eq. (13.63) gives

$$5 e = 0.68888 (14.163)$$

The nucleus of the C atoms comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{ethane}2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{ethane}2sp^3 = 0.87495a_0$  is the radius of the  $C_{ethane}2sp^3$  shell.

10 Substitution of Eqs. (14.158-14.159) into Eq. (13.261) gives

$$\theta' = 67.33^{\circ}$$
 (14.164)

Then, the angle  $\theta_{C-C_{ethaus}}$   $^{2sp^3}HO$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C-C_{A-1}-2sp^3HO} = 180^{\circ} - 67.33^{\circ} = 112.67^{\circ}$$
(14.165)

15 as shown in Figure 37.

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-C_{\text{ethans}},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -

20 type ellipsoidal MO with the  $C_{ethanse} 2sp^3$  radial vector obeys the following relationship:

$$r_{ethane 2sp^3} \sin \theta_{C-C_{ethane 2sp^3HO}} = 0.87495 a_0 \sin \theta_{C-C_{ethane 2sp^3HO}} = b \sin \theta_{C-C_{ethane 1}, H_2MO}$$
 (14.166)

such that

$$\theta_{C-C_{ethoms}, H_2MO} = \sin^{-1} \frac{0.87495 a_0 \sin \theta_{C-C_{ethoms}} 2sp^3 HO}{h} = \sin^{-1} \frac{0.87495 a_0 \sin 112.67^{\circ}}{h}$$
 (14.167)

with the use of Eq. (14.166). Substitution of Eq. (14.162) into Eq. (14.167) gives

$$\theta_{C-C_{\text{othorw}}, H_2MO} = 31.91^{\circ} \tag{14.168}$$

Then, the distance  $d_{C-C_{cham},H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-C_{cham},H_2MO} = a\cos\theta_{C-C_{cham},H_2MO} \tag{14.169}$$

Substitution of Eqs. (14.158) and (14.168) into Eq. (14.169) gives

$$d_{C-C_{ethano},H_2MO} = 1.78885a_0 = 9.46617 X 10^{-11} m {(14.170)}$$

The distance  $d_{C-C_{nlker},2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-C_{\text{others}} 2sp^3HO} = d_{C-C_{\text{others}}, H_2MO} - c^{1}$$
(14.171)

5 Substitution of Eqs. (14.159) and (14.170) into Eq. (14.171) gives

$$d_{C-C_{\text{chase}}, 2sp^3HO} = 0.33721a_0 = 1.78444 \ X \ 10^{-11} \ m \tag{14.172}$$

# FORCE BALANCE OF THE CH<sub>3</sub> MOs OF ETHANE

Each of the two equivalent  $CH_3$  MOs must comprise three C-H bonds with each 10 comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO as given by Eq. (13.540):

$$3[1 C2sp^3 + 0.75 H_2 MO] \rightarrow CH_3 MO$$
 (14.173)

The force balance of the  $CH_3$  MO is determined by the boundary conditions that arise from 15 the linear combination of orbitals according to Eq. (13.540) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH_3$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each C-H-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each C-H-bond MO. Since each of the three prolate spheroidal C-H-bond MOs comprises an  $H_2$ -type-ellipsoidal MO that transitions to the  $C_{ethane}2sp^3$  HO of ethane, the energy  $E\left(C_{ethane},2sp^3\right)$  of Eq. (14.150) adds to that of the three corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_3$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_3$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ , T, and  $V_m$  are the same as those of methyl radical, three times those of CH corresponding to the three C-H bonds except that energy of the  $C_{ethane} 2sp^3$  HO is used. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C_{ethane} 2sp^3$  HO and the energy of the  $C_{ethane} 2sp^3$  shell must remain constant and equal to the  $E\left(C_{ethane}, 2sp^3\right)$  given by Eq. (14.150), the total energy  $E_{T_{ethane}}\left(CH_3\right)$  of the  $CH_3$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C_{ethane} 2sp^3$  HO and the three  $H_2$ -type ellipsoidal MOs that forms the  $CH_3$  MO as given by Eq. (13.540). Using Eq. (13.431),  $E_{T_{ethane}}\left(CH_3\right)$  is given by

$$E_{T_{ethanse}}(CH_3) = E_T + E(C_{ethanse}, 2sp^3)$$

$$= -\frac{3e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 15.35946 \, eV$$
(14.174)

10  $E_{T_{char}}(CH_3)$  given by Eq. (14.174) is set equal to three times the energy of the  $H_2$ -type ellipsoidal MO minus two times the Coulombic energy of H given by Eq. (13.542):

$$E_T(CH_3) = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 15.35946 \ eV = -67.69450 \ eV$$
 (14.175)

From the energy relationship given by Eq. (14.175) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_3$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.175) gives

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e52.33505$$
 (14.176)

The most convenient way to solve Eq. (14.176) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$20 a = 1.64469a_0 = 8.70331 X 10^{-11} m (14.177)$$

Substitution of Eq. (14.177) into Eq. (14.60) gives

$$c' = 1.04712a_0 = 5.54111 \times 10^{-11} m \tag{14.178}$$

The internuclear distance given by multiplying Eq. (14.178) by two is

$$2c' = 2.09424a_0 = 1.10822 \ X \ 10^{-10} \ m \tag{14.179}$$

25 The experimental bond distance is [3]

$$2c' = 1.0940 \ X \ 10^{-10} \ m \tag{14.180}$$

Substitution of Eqs. (14.177-14.178) into Eq. (14.62) gives

$$b = c = 1.26828a_0 = 6.71145 \ X \ 10^{-11} \ m \tag{14.181}$$

Substitution of Eqs. (14.177-14.178) into Eq. (14.63) gives

$$5 e = 0.63667 (14.182)$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{ethane} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{ethane2:p^3} = 0.87495a_0$  is the radius of the  $C_{ethane} 2sp^3$  shell. Substitution of Eqs. (14.177-14.178) into Eq. (13.261) gives

$$\theta' = 79.34^{\circ}$$
 (14.183)

Then, the angle  $\theta_{C-H_{ethans}}^{2sp^3}HO$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

15 
$$\theta_{C-H_{\text{then}},2sp^3HO} = 180^{\circ} - 79.34^{\circ} = 100.66^{\circ}$$
 (14.184)

as shown in Figure 38.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{ethors},H_2MO}$  between the 20 internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{ethors} 2sp^3$  radial vector obeys the following relationship:

$$r_{ethane 2sp^3} \sin \theta_{C-H_{ethane }2sp^3HO} = 0.87495a_0 \sin \theta_{C-H_{ethane }2sp^3HO} = b \sin \theta_{C-H_{ethane },H_{2}MO}$$
 (14.185)

such that

$$\theta_{C-H_{ethane},H_2MO} = \sin^{-1} \frac{0.87495a_0 \sin \theta_{C-H_{ethane} 2sp^3HO}}{b} = \sin^{-1} \frac{0.87495a_0 \sin 100.66^{\circ}}{b}$$
 (14.186)

25 with the use of Eq. (14.184). Substitution of Eq. (14.181) into Eq. (14.186) gives

$$\theta_{C-H_{chang}, H_2MO} = 42.68^{\circ} \tag{14.187}$$

Then, the distance  $d_{C-H_{athons},H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{\text{-thoms}},H_{2}MO} = a\cos\theta_{C-H_{\text{-thoms}},H_{2}MO} \tag{14.188}$$

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Substitution of Eqs. (14.177) and (14.187) into Eq. (14.188) gives

$$d_{C-H_{ethems},H_2MO} = 1.20901a_0 = 6.39780 X 10^{-11} m (14.189)$$

The distance  $d_{C-H_{ethan},2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{chore} 2.sp^3HO} = d_{C-H_{ethore}, H_2MO} - c'$$
 (14.190)

Substitution of Eqs. (14.178) and (14.189) into Eq. (14.190) gives

$$d_{C-H_{classes} 2sp^3HO} = 0.16189a_0 = 8.56687 X 10^{-12} m$$
 (14.191)

## BOND ANGLE OF THE CH, GROUPS

Each CH<sub>3</sub> MO comprises a linear combination of three C-H-bond MOs. Each C-H-bond MO comprises the superposition of a H<sub>2</sub>-type ellipsoidal MO and the C<sub>ethane</sub> 2sp³ HO. A bond is also possible between the two H atoms of the C-H bonds. Such H-H bonding would decrease the C-H bond strength since electron density would be shifted from the C-H bonds to the H-H bond. Thus, the bond angle between the two C-H bonds is determined by the condition that the total energy of the H<sub>2</sub>-type ellipsoidal MO between the terminal H atoms of the C-H bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the H-H ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{14.192}$$

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.193}$$

The length of the semiminor axis of the prolate spheroidal H-H MO b=c is given by Eq. (14.62).

The bond angle of the  $CH_3$  groups of ethane is derived by using the orbital composition and an energy matching factor as in the case with the  $CH_3$  radical. Since the 25 two  $H_2$ -type ellipsoidal MOs initially comprise 75% of the H electron density of  $H_2$  and the energy of each  $H_2$ -type ellipsoidal MO is matched to that of the  $C_{ethane}2sp^3$  HO, the component energies and the total energy  $E_T$  of the H-H bond are given by Eqs. (13.67-13.73) except that  $V_e$ , T, and  $V_m$  are corrected for the hybridization-energy-matching factor

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of 0.87495. Hybridization with 25% electron donation to the C-C-bond gives rise to the  $C_{ethans} 2sp^3$  HO-shell Coulombic energy  $E_{Coulomb} (C_{ethans}, 2sp^3)$  given by Eq. (14.149). The corresponding normalization factor for determining the zero of the total H-H bond energy is given by the ratio of 15.55033 eV, the magnitude of  $E_{Coulomb}(C_{ethane}, 2sp^3)$  given by Eq. 5 (14.149), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The hybridization energy factor  $C_{ethaneC2sp^3HO}$  is

$$C_{ethaneC2sp^{3}HO} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{ethane2sp^{3}}}} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}0.87495a_{0}}} = \frac{13.605804 \, eV}{15.55033 \, eV} = 0.87495 \quad (14.194)$$

Substitution of Eq. (14.152) into Eq. (13.233) with the hybridization factor of 0.87495 gives

Substitution of Eq. (14.132) into Eq. (13.233) with the hypothesistant late 
$$0.87495$$
 gives
$$0 = \begin{bmatrix} \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left[ (0.87495)^{-1} \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 a^3}}}{\frac{m_e}{m_e c^2}}} \right] + \hbar\sqrt{\frac{0.75e^2}{8\pi\varepsilon_0 a^3} \frac{e^2}{8\pi\varepsilon_0 (a + c^3)^3}}$$
(14.195)

From the energy relationship given by Eq. (14.195) and the relationship between the axes given by Eqs. (14.192-14.193) and (14.62-14.63), the dimensions of the H-H MO can be solved.

The most convenient way to solve Eq. (14.195) is by the reiterative technique using a 15 computer. The result to within the round-off error with five-significant figures is

$$a = 5.7000a_0 = 3.0163 \ X \ 10^{-10} \ m \tag{14.196}$$

Substitution of Eq. (14.196) into Eq. (14.192) gives

$$c' = 1.6882a_0 = 8.9335 X 10^{-11} m (14.197)$$

20 The internuclear distance given by multiplying Eq. (14.197) by two is

$$2c' = 3.3764a_0 = 1.7867 \ X \ 10^{-10} \ m \tag{14.198}$$

Substitution of Eqs. (14.196-14.197) into Eq. (14.62) gives

$$b = c = 5.4443a_0 = 2.8810 X 10^{-10} m ag{14.199}$$

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Substitution of Eqs. (14.196-14.197) into Eq. (14.63) gives

$$e = 0.2962 \tag{14.200}$$

From,  $2c'_{H-H}$  (Eq. (14.198)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (14.195)), and  $2c'_{C-H}$  (Eq. (14.179)), the 5 internuclear distance of each C-H bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle  $\theta$  between the C-H bonds is

$$\theta = \cos^{-1}\left(\frac{2(2.09424)^2 - (3.3764)^2}{2(2.09424)^2}\right) = \cos^{-1}\left(-0.29964\right) = 107.44^{\circ}$$
 (14.201)

The experimental angle between the C-H bonds is [8]

$$\theta = 107.4^{\circ}$$
 (14.202)

The  $CH_3$  radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance  $d_{origin-H}$  from the origin to the nucleus of a hydrogen atom given by Eqs. (14.198) and (13.412) is

$$d_{\text{origin-H}} = 1.94936a_0 \tag{14.203}$$

The height along the z-axis of the pyramid from the origin to C nucleus  $d_{height}$  given by Eqs.

15 (13.414), (14.179), and (14.203) is

$$d_{height} = 0.76540a_0 \tag{14.204}$$

The angle  $\theta_r$  of each C-H bond from the z-axis given by Eqs. (13.416), (14.203), and (14.204) is

$$\theta_{\nu} = 68.563^{\circ}$$
 (14.205)

20 The C-C bond is along the z-axis. Thus, the bond angle  $\theta_{C-C-H}$  between the internuclear axis of the C-C bond and a H atom of the methyl groups is given by

$$\theta_{C-C-H} = 180 - \theta_{v} \tag{14.206}$$

Substitution of Eq. (14.205) into Eq. (14.206) gives

$$\theta_{C-C-H} = 111.44^{\circ} \tag{14.207}$$

25 The experimental angle between the C-C-H bonds is [3]

$$\theta_{C-C-H} = 111.17^{\circ} \tag{14.208}$$

The  $CH_3CH_3$  MO shown in Figure 39 was rendered using these parameters. A minimum energy is obtained with a staggered configuration consistent with observations [3].

The charge-density in the C-C-bond MO is increased by a factor of 0.25 with the formation of the  $C_{ethane} 2sp^3$  HOs each having a smaller radius. Using the orbital composition of the  $CH_3$  groups (Eq. (14.173)) and the C-C-bond MO (Eq. (14.139), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C_{ethane} 2sp^3 = 0.87495a_0$  (Eq. (14.148)) shells, and the 5 parameters of the C-C-bond (Eqs. (13.3-13.4), (14.158-14.160), and (14.162-14.172)), the parameters of the C-H-bond MOs (Eqs. (13.3-13.4), (14.177-14.179), and (14.181-14.191)), and the bond-angle parameters (Eqs. (14.195-14.208)), the charge-density of the  $CH_3CH_3$  MO comprising the linear combination of two sets of three C-H-bond MOs and a C-C-bond MO bridging the two methyl groups is shown in Figure 39. Each C-H-bond 10 MO comprises a  $H_2$ -type ellipsoidal MO and a  $C_{ethane} 2sp^3$  HO having the dimensional diagram shown in Figure 38. The C-C-bond MO comprises a  $H_2$ -type ellipsoidal MO bridging two  $C_{ethane} 2sp^3$  HOs having the dimensional diagram shown in Figure 37.

### ENERGIES OF THE CH, GROUPS

The energies of each  $CH_3$  group of ethane are given by the substitution of the semiprincipal axes (Eqs. (14.177-14.178) and (14.181)) into the energy equations of the methyl radical (Eqs. (13.556-13.560)), with the exception that  $E(C_{ethane}, 2sp^3)$  replaces  $E(C, 2sp^3)$  in Eq. (13.560):

$$V_e = 3(0.91771) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -107.68424 \ eV$$
 (14.209)

$$V_p = \frac{3e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 38.98068 \ eV \tag{14.210}$$

20 
$$T = 3(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 32.73700 \ eV$$
 (14.211)

$$V_{m} = 3(0.91771) \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -16.36850 \ eV$$
 (14.212)

$$E_{T_{channel}}(CH_3) = -\frac{3e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 15.35946 \ eV = -67.69451 \ eV$$
(14.213)

where  $E_{T_{efficient}}$  (CH<sub>3</sub>) is given by Eq. (14.174) which is reiteratively matched to Eq. (13.542) within five-significant-figure round off error.

#### VIBRATION OF THE 12CH, GROUPS

The vibrational energy levels of  $CH_3$  in ethane may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE 12CH3 GROUPS

10 The equations of the radiation reaction force of the methyl groups in ethane are the same as those of the methyl radical with the substitution of the methyl-group parameters. Using Eq. (13.561), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 2.50664 \times 10^{16} \text{ rad/s}$$
 (14.214)

where b is given by Eq. (14.181). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. 15 (11.127)):

$$\overline{E}_K = \hbar \omega = \hbar 2.50664 \, X \, 10^{16} \, rad \, / \, s = 16.49915 \, eV$$
 (14.215)

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.215) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the 20 three bonds for the reentrant orbit:

$$\overline{E}_{D} \cong E_{h\nu} \sqrt{\frac{2\overline{E}_{K}}{Mc^{2}}} = -31.63537 \ eV \sqrt{\frac{2e\left(16.49915 \ eV\right)}{m_{e}c^{2}}} = -0.25422 \ eV \tag{14.216}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH_3$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{asc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (14.216) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which

is 1/2 of the vibrational energy of each C-H bond. Using  $\omega_e$  given by Eq. (13.458) for  $\overline{E}_{K\nu lb}$  of the transition state having three independent bonds,  $\overline{E}_{ethane\ osc}^{\prime}\left({}^{12}CH_3\right)$  per bond is

$$\overline{E}'_{ethane \ osc} \left(^{12}CH_3\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(14.217)

$$\overline{E}_{elhane\ osc}^{\prime}(^{12}CH_3) = -0.25422\ eV + \frac{1}{2}(0.35532\ eV) = -0.07656\ eV$$
 (14.218)

5 Given that the vibration and reentrant oscillation is for three C-H bonds,  $\overline{E}_{ethane\ osc}(^{12}CH_3)$ , is:

$$\overline{E}_{ethane \, osc} \left( {}^{12}CH_3 \right) = 3 \left( \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) 
= 3 \left( -0.25422 \, eV + \frac{1}{2} (0.35532 \, eV) \right) 
= -0.22967 \, eV$$
(14.219)

## TOTAL AND DIFFERENCE ENERGIES OF THE 12CH, GROUPS

10  $E_{ethameT+osc}(^{12}CH_3)$ , the total energy of each  $^{12}CH_3$  group including the Doppler term, is given by the sum of  $E_{T_{ethame}}(CH_3)$  (Eq. (14.213)) and  $\overline{E}_{ethame \, osc}(^{12}CH_3)$  given by Eq. (14.219):

$$E_{ethaneT+osc}(CH_3) = V_e + T + V_m + V_p + E(C_{ethone}, 2sp^3) + \overline{E}_{ethane\ osc}(^{12}CH_3)$$

$$= E_{T_{ethane}}(CH_3) + \overline{E}_{ethane\ osc}(^{12}CH_3)$$
(14.220)

$$E_{ethaneT+osc}(^{12}CH_{3}) = \begin{cases} \left(\frac{-3e^{2}}{8\pi\varepsilon_{0}c'}\right[(0.91771)\left(2-\frac{1}{2}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.359469 eV) \\ \left(\frac{12}{3}\left(31.63536831 eV\right)\sqrt{\frac{3}{2}\frac{e^{2}}{44\pi\varepsilon_{0}b^{3}}} -\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \\ = -67.69450 eV - 3\left(0.25422 eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{cases}$$
(14.221)

From Eqs. (14.217-14.221), the total energy of each  $^{12}CH_3$  is

$$E_{ethameT+osc} {12CH_3} = -67.69450 \ eV + \overline{E}_{ethame \ osc} {12CH_3}$$

$$= -67.69450 \ eV - 3 \left( 0.25422 \ eV - \frac{1}{2} (0.35532 \ eV) \right)$$

$$= -67.92417 \ eV$$
(14.222)

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The total energy for each methyl radical given by Eq. (13.569) is

$$\begin{split} E_{radicalT+osc}\left(^{12}CH_{3}\right) &= -67.69450 \ eV + \overline{E}_{radical \ osc}\left(^{12}CH_{3}\right) \\ &= -67.69450 \ eV - 3\bigg(0.25670 \ eV - \frac{1}{2}\big(0.35532 \ eV\big)\bigg) \\ &= -67.93160 \ eV \end{split} \tag{14.223}$$

5 The difference in energy between the methyl groups and the methyl radical  $\Delta E_{T+asc}(^{12}CH_3)$  is given by two times the difference between Eqs. (14.222) and (14.223):

$$\Delta E_{T+osc} \left( {}^{12}CH_3 \right) = 2 \left( E_{elhameT+osc} \left( {}^{12}CH_3 \right) - E_{radicalT+osc} \left( {}^{12}CH_3 \right) \right)$$

$$= 2 \left( -67.92417 \ eV - \left( -67.93160 \ eV \right) \right)$$

$$= 0.01487 \ eV$$
(14.224)

SUM OF THE ENERGIES OF THE C-C  $\sigma$  MO AND THE HOS OF 10 ETHANE

The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of the C-C-bond MO are the same as those of the CH MO as well as each C-H-bond MO of the methyl groups except that energy of the  $C_{ethane} 2sp^3$  HO is used. The energies of each C-C-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.158-14.159) and (14.162)) into the energy equations of the CH MO (Eqs. (13.449-13.453)), with the exception that  $E\left(C_{ethane}, 2sp^3\right)$  replaces  $E\left(C, 2sp^3\right)$  in Eq. (13.453):

$$V_{e} = (0.91771) \frac{-2e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} = -29.101124 \ eV$$
 (14.225)

$$V_{p} = \frac{e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} = 9.37273 \ eV \tag{14.226}$$

$$T = (0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 6.90500 \ eV$$
 (14.227)

$$V_m = (0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{344}{a - \sqrt{a^2 - b^2}} = -3.45250 \ eV$$
 (14.228)

$$E_{T}(C-C,\sigma) = -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \ eV = -31.63535 \ eV$$

$$(14.229)$$

where  $E_T(C-C,\sigma)$  is the total energy of the C-C  $\sigma$  MO given by Eq. (14.155) which is 5 reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

The total energy of the C-C-bond MO,  $E_T(C-C)$ , is given by the sum of two times  $E_T(C-C,2sp^3)$ , the energy change of each  $C2sp^3$  shell due to the decrease in radius with the formation of the C-C-bond MO (Eq. (14.151)), and  $E_T(C-C,\sigma)$ , the  $\sigma$  MO contribution given by Eq. (14.156):

$$E_{T}(C-C) = 2E_{T}(C-C,2sp^{3}) + E_{T}(C-C,\sigma)$$

$$= \begin{pmatrix} 2(-0.72457 \ eV) + \\ -\frac{e^{2}}{8\pi\varepsilon_{0}\sqrt{aa_{0}}} \left[ (0.91771)\left(2 - \frac{1}{2} \frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{aa_{0}}}{a - \sqrt{aa_{0}}} - 1\right] - 15.35946 \ eV \end{pmatrix} (14.230)$$

$$= 2(-0.72457 \ eV) + (-31.63537 \ eV)$$

$$= -33.08452 \ eV$$

#### VIBRATION OF ETHANE

The vibrational energy levels of  $CH_3CH_3$  may be solved as two sets of three equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE C-C-BOND MO OF ETHANE

20 The equations of the radiation reaction force of the symmetrical C-C-bond MO are given by Eqs. (11.231-11.233), except the force-constant factor is 0.5 based on the force constant k' of Eq. (14.152), and the C-C-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.5e^2}{4\pi\varepsilon_0 a^3}} = 9.55643 \, X \, 10^{15} \, rad/s \tag{14.231}$$

where a is given by Eq. (14.158). The kinetic energy,  $E_{\kappa}$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_{\kappa} = \hbar \omega = \hbar 9.55643 \, X \, 10^{15} \, rad \, / \, s = 6.29021 \, eV$$
 (14.232)

5 In Eq. (11.181), substitution of  $E_T(C-C)$  (Eq. (14.230)) for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.232) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -33.08450 \ eV \sqrt{\frac{2e(6.29021 \ eV)}{m_e c^2}} = -0.16416 \ eV \tag{14.233}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the C-C-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (14.233) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of the C-C bond. Using the experimental 15 C-C  $E_{vib}(v_3)$  of 993  $cm^{-1}$  (0.12312 eV) [10] for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{osc}(C-C,\sigma)$  is

$$\overline{E}_{osc}(C-C,\sigma) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(14.234)

$$\overline{E}_{osc}(C-C,\sigma) = -0.16416 \ eV + \frac{1}{2}(0.12312 \ eV) = -0.10260 \ eV$$
 (14.235)

#### 20 TOTAL ENERGIES OF THE C-C-BOND MO OF ETHANE

 $E_{T+osc}(C-C)$ , the total energy of the C-C-bond MO including the Doppler term, is given by the sum of  $E_T(C-C)$  (Eq. (14.230)) and  $\overline{E}_{osc}(C-C,\sigma)$  given by Eq. (14.235):

$$E_{T+osc}(C-C) = V_{e} + T + V_{m} + V_{p} + E(C_{ethane}, 2sp^{3}) + 2E_{T}(C-C, 2sp^{3}) + \overline{E}_{osc}(C-C, \sigma)$$

$$= E_{T}(C-C, \sigma) + 2E_{T}(C-C, 2sp^{3}) + \overline{E}_{osc}(C-C, \sigma)$$

$$= E_{T}(C-C) + \overline{E}_{osc}(C-C, \sigma)$$

$$= \left\{ \left( \frac{-e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.35946 \ eV + 2E_{T}(C-C, 2sp^{3}) \right\} \right\}$$

$$E_{T+osc}(C-C) = \left\{ \left( \frac{2\hbar\sqrt{\frac{1}{2} \frac{e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{1 + \sqrt{\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}}} \right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\}$$

$$\left( 1 + \sqrt{\frac{m_e}{m_e c^2}} \right) = -33.08452 \, eV - 0.16416 \, eV + \frac{1}{2} \, \hbar \sqrt{\frac{k}{\mu}}$$
(14.237)

5 From Eqs. (14.234-14.237), the total energy of the C-C-bond MO is

$$E_{T+osc}(C-C) = -31.63537 \ eV + 2E_T(C-C,2sp^3) + \overline{E}_{osc}(C-C,\sigma)$$

$$= -31.63537 \ eV + 2(-0.72457 \ eV) - 0.16416 \ eV + \frac{1}{2}(0.12312 \ eV) \qquad (14.238)$$

$$= -33.18712 \ eV$$

where the experimental  $E_{vib}$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

#### BOND ENERGY OF THE C-C BOND OF ETHANE

10 The dissociation energy of the C-C bond of  $CH_3CH_3$ ,  $E_D\left(H_3C-CH_3\right)$ , is given by two times  $E\left(C,2sp^3\right)$  (Eq. (14.146)), the initial energy of the  $C2sp^3$  HO of each  $CH_3$  radical that bond with a single C-C bond, minus the sum of  $\Delta E_{T+asc}\left(^{12}CH_3\right)$  (Eq. (14.224)), the energy change going from the methyl radicals to the methyl groups of ethane, and  $E_{T+asc}\left(C-C\right)$  (Eq. (14.238)). Thus, the dissociation energy of the C-C bond of  $CH_3CH_3$ ,

15 is

$$E_{D}(H_{3}C - CH_{3}) = 2(E(C, 2sp^{3})) - (\Delta E_{T+osc}(^{12}CH_{3}) + E_{T+osc}(C - C))$$

$$= 2(-14.63489 eV) - (0.01487 eV - 33.18712 eV)$$

$$= 2(-14.63489 eV) - (33.17225 eV)$$

$$= 3.90247 eV$$
(14.239)

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The experimental dissociation energy of the C-C bond of  $CH_3CH_3$  is [6]

$$E_D(H_3C - CH_3) = 3.89690 \ eV \tag{14.240}$$

The results of the determination of bond parameters of  $CH_3CH_3$  are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact 5 equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

# ETHYLENE MOLECULE (CH2CH2)

The ethylene molecule  $CH_2CH_2$  is formed by the reaction of two dihydrogen carbide 10 radicals:

$$CH_2 + CH_2 \rightarrow CH_2CH_2 \tag{14.241}$$

CH<sub>2</sub>CH<sub>2</sub> can be solved using the same principles as those used to solve the methane series
CH<sub>n=1,2,3,4</sub>, wherein the 2s and 2p shells of each C hybridize to form a single 2sp³ shell as an energy minimum, and the sharing of electrons between two C2sp³ hybridized orbitals
(HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of two H atomic orbitals (AOs) combine with two sets of two carbon 2sp³ HOs to form two dihydrogen carbide groups comprising a linear combination of four diatomic H<sub>2</sub>-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two CH<sub>2</sub> groups bond by
forming a H<sub>2</sub>-type MO between the remaining two C2sp³ HOs on each carbon atom.

## FORCE BALANCE OF THE C = C-BOND MO OF ETHYLENE

 $CH_2CH_2$  comprises a chemical bond between two  $CH_2$  radicals wherein each radical comprises two chemical bonds between carbon and hydrogen atoms. The solution of the parameters of  $CH_2$  is given in the Dihydrogen Carbide  $(CH_2)$  section. Each C-H bond of  $CH_2$  having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , each of

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the two C-H-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the  $C2sp^3$  shell at the C atom whose nucleus serves as the other focus. The electron configuration and the energy,  $E(C,2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each C-H bond is provided by the spin-pairing force of the  $CH_2$  MO that has the symmetry of an s orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged.

Two  $CH_2$  radicals bond to form  $CH_2CH_2$  by forming a MO between the two pairs of remaining  $C2sp^3$ -HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between four  $C2sp^3$  HOs to form a molecular orbital (MO) comprising four spin-paired electrons permits each  $C2sp^3$  HO to decrease in radius and energy.

As in the case of the C-H bonds, the C=C-bond MO is a prolate-spheroidal-MO surface that cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the  $C2sp^3$  shell at each C atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  shell. As in the case of previous examples of energy-matched MOs such as those of OH, NH, CH, the C=O-bond MO of  $CO_2$ , and the C-C-bond MO of  $CH_3CH_3$ , the C=C-bond MO of ethylene must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the C=C-bond MO must comprise a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

25

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$$2(2 C2sp^3 + 0.75 H_2 MO) \rightarrow C = C - bond MO$$
 (14.242)

The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution from each  $C2sp^3$  HO to the C=C-

bond MO to achieve an energy minimum. The force balance of the C = C-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.242) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

- Similarly, the energies of each  $CH_2$  MO involve each  $C2sp^3$  and each H1s electron with the formation of each C-H bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. This energy is determined by the considering the effect of the donation of 25% electron density from the two pairs of  $C2sp^3$  HOs to the C=C-bond MO with the formation of the  $C_{ethylene}2sp^3$  HOs each having a smaller radius.

  10 The  $2sp^3$  hybridized orbital arrangement is given by Eq. (14.140). The sum  $E_T(C,2sp^3)$  of calculated energies of C,  $C^*$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.141). The radius  $r_{2m^3}$  of the
  - calculated energies of C,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.141). The radius  $r_{2sp}$ , of the  $C2sp^3$  shell is given by Eq. (14.142). The Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  and the energy  $E(C, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell are given by Eqs. (14.143) and (14.146), respectively.
- Next, consider the formation of the C=C-bond MO of ethylene from two  $CH_2$  radicals, each having a  $C2sp^3$  electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum  $E_T\left(C_{ethylene}, 2sp^3\right)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$E_T(C_{ethylene}, 2sp^3) = -(64.3921 \ eV + 48.3125 \ eV + 24.2762 \ eV + E(C, 2sp^3))$$

$$= -(64.3921 \ eV + 48.3125 \ eV + 24.2762 \ eV + 14.63489 \ eV)$$

$$= -151.61569 \ eV$$

(14.243)

where  $E(C,2sp^3)$  (Eq. (14.146)) is the sum of the energy of C,  $-11.27671\,eV$ , and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the  $E_T(C_{elbplene},2sp^3)$  is purely Coulombic.

The sharing of electrons between two pairs of  $C2sp^3$  HOs to form a C=C-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating

 $C2sp^3$  HO donates an excess of 25% per bond of its electron density to the C=C-bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{ethylene2sp}$  of the  $C2sp^3$  shell of ethylene may be calculated

$$r_{ethylene2sp^3} = \left(\sum_{n=2}^{5} (Z-n) - 0.5\right) \frac{e^2}{8\pi\varepsilon_0 \left(e151.61569 \, eV\right)} = \frac{9.5e^2}{8\pi\varepsilon_0 \left(e151.61569 \, eV\right)} = 0.85252a_0 \tag{14.244}$$

5 from the Coulombic energy using Eq. (10.102):

15

where Z=6 for carbon. Using Eqs. (10.102) and (14.244), the Coulombic energy  $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$  of the outer electron of the  $C2sp^3$  shell is

10 
$$E_{Coulomb}\left(C_{ethylene}, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{ethylene2sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.85252a_{0}} = -15.95955 \,eV \qquad (14.245)$$

During hybridization, one of the spin-paired 2s electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.245), the energy  $E(C_{ethylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E(C_{ethylene}, 2sp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{ethylene2sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(r_{3})^{3}}$$

$$= -15.95955 \ eV + 0.19086 \ eV$$

$$= -15.76868 \ eV$$
(14.246)

Thus,  $E_T(C=C,2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of the C=C-bond MO is given by the difference between Eq. (14.146) and Eq. (14.246):

$$E_{T}(C = C, 2sp^{3}) = E(C_{ethylene}, 2sp^{3}) - E(C, 2sp^{3})$$

$$= -15.76868 \ eV - (-14.63489 \ eV)$$

$$= -1.13380 \ eV$$
(14.247)

As in the case of  $Cl_2$ , each  $H_2$ -type ellipsoidal MO comprises 75% of the C=C-bond MO shared between two  $C2sp^3$  HOs corresponding to the electron charge density in Eq. (11.65) of  $\frac{-0.75e}{2}$ . But, the additional 25% charge-density contribution to each bond of the C=C-bond MO causes the electron charge density in Eq. (11.65) to be is given by  $\frac{-e}{2}=-0.5e$ . The

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corresponding force constant k' is given by Eq. (14.152). In addition, the energy matching at both  $C2sp^3$  HOs further requires that k' be corrected by the hybridization factor given by Eq. (13.430). Thus, the force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci (Eq. (11.65)) is given by

5 
$$k' = C_{C2sp^3HO} \frac{(0.5)2e^2}{4\pi\varepsilon_0} = 0.91771 \frac{(0.5)2e^2}{4\pi\varepsilon_0}$$
 (14.248)

The distance from the origin to each focus c' is given by substitution of Eq. (14.248) into Eq. (13.60). Thus, the distance from the origin of the component of the double C = C-bond MO to each focus c' is given by

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{(0.91771)m_e^2 a}} = \sqrt{\frac{aa_0}{0.91771}}$$
(14.249)

10 The internuclear distance from Eq. (14.249) is

$$2c' = 2\sqrt{\frac{aa_0}{0.91771}}\tag{14.250}$$

The length of the semiminor axis of the prolate spheroidal C = C-bond MO b = c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the C = C-bond MO. From the energy equation and the relationship between the axes, the dimensions of the C = C-bond MO are solved.

The general equations for the energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of the C=C-bond MO are the same as those of the CH MO except that energy of the  $C_{ethylene}2sp^3$  HO is used and the double-bond nature is considered. In the case of a single bond, the prolate spheroidal  $H_2$ -type MO transitions to the  $C_{ethylene}2sp^3$  HO of each carbon, and the energy of the  $C_{ethylene}2sp^3$  shell must remain constant and equal to the  $E\left(C_{ethylene},2sp^3\right)$  given by Eq. (14.246). Thus, the energy  $E\left(C_{ethylene},2sp^3\right)$  in Eq. (14.246) adds to that of the energies of the corresponding  $H_2$ -type ellipsoidal MO. The second bond of the double C=C-bond MO also transitions to the  $C_{ethylene}2sp^3$  HO of each C. The energy of a second  $H_2$ -type ellipsoidal MO adds to the first energy component, and the two bonds achieve an energy minimum as a linear combination of the two  $H_2$ -type ellipsoidal MOs each having the carbon nuclei as the foci. Each C-C-bond MO comprises the same  $C_{ethylene}2sp^3$  HO shells of

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constant energy given by Eq. (14.246). As in the case of the water,  $NH_2$ , and ammonia molecules given by Eqs. (13.180), (13.320), and (13.372), respectively, the energy of the redundant shell is subtracted from the total energy of the linear combination of the  $\sigma$  MO. Thus, the total energy  $E_T(C=C,\sigma)$  of the  $\sigma$  component of the C=C-bond MO is given by the sum of the energies of the two bonds each comprising the linear combination of the  $C_{ethylene}2sp^3$  HO and the  $H_2$ -type ellipsoidal MO as given by Eq. (14.242) wherein the  $E_T$  terms add positively, the  $E(C_{ethylene}, 2sp^3)$  terms cancel, and the energy matching condition between the components is provided by Eq. (14.248). Using Eqs. (13.431) and (14.246),  $E_T(C=C,\sigma)$  is given by

$$E_{T}(C = C, \sigma) = E_{T} + E(C_{ethylene}, 2sp^{3}) - E(C_{ethylene}, 2sp^{3})$$

$$= -\frac{2e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right]$$
(14.251)

The total energy term of the double C = C-bond MO is given by the sum of the two  $H_2$ -type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition,  $E_T(C = C, \sigma)$  given by Eq. (14.251) is set equal to two times Eq. (13.75):

$$E_T(C=C,\sigma) = -\frac{2e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] = -63.27074 \ eV$$
 (14.252)

15 From the energy relationship given by Eq. (14.252) and the relationship between the axes given by Eqs. (14.249-14.250) and (13.62-13.63), the dimensions of the C = C-bond MO can be solved.

Substitution of Eq. (14.249) into Eq. (14.252) gives

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{0.91771}}} \left[ (0.91771)\left(2 - \frac{1}{2}\frac{a_0}{a}\right) \ln\frac{a + \sqrt{\frac{aa_0}{0.91771}}}{a - \sqrt{\frac{aa_0}{0.91771}}} - 1 \right] = e63.27074 \qquad (14.253)$$

20 The most convenient way to solve Eq. (14.253) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.47228a_0 = 7.79098 X 10^{-11} m ag{14.254}$$

Substitution of Eq. (14.254) into Eq. (14.249) gives

$$c' = 1.26661a_0 = 6.70259 X 10^{-11} m (14.255)$$

25 The internuclear distance given by multiplying Eq. (14.255) by two is

$$2c' = 2.53321a_0 = 1.34052 X 10^{-10} m ag{14.256}$$

The experimental bond distance is [3]

$$2c' = 1.339 \ X \ 10^{-10} \ m \tag{14.257}$$

Substitution of Eqs. (14.254-14.255) into Eq. (13.62) gives

$$b = c = 0.75055a_0 = 3.97173 \times 10^{-11} m \tag{14.258}$$

Substitution of Eqs. (14.252-14.255) into Eq. (13.63) gives

$$e = 0.86030 \tag{14.259}$$

The nucleus of the C atoms comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{ethylene}2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{ethylene2sp^3} = 0.85252a_0$  is the radius of the  $C_{ethylene}2sp^3$  shell. Substitution of Eqs. (14.254-14.255) into Eq. (13.261) gives

$$\theta' = 129.84^{\circ}$$
 (14.260)

Then, the angle  $\theta_{C=C_{ethylene}2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear

$$\theta_{C=C_{\text{thicker}} 2sp^3HO} = 180^{\circ} - 129.84^{\circ} = 50.16^{\circ}$$
 (14.261)

as shown in Figure 40.

15 axis is

Consider the right-hand intersection point. The distance from the point of intersection of the 20 orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C=C_{abplices},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with each  $C_{elloulene} 2sp^3$  radial vector obeys the following relationship:

$$r_{ethylene2sp^3} \sin \theta_{C=C_{ethylene}2sp^3HO} = 0.85252a_0 \sin \theta_{C=C_{ethylene}2sp^3HO} = b \sin \theta_{C=C_{ethylene},H_2MO}$$
 (14.262) such that

25 
$$\theta_{C=C_{cllydrin},H_2MO} = \sin^{-1} \frac{0.85252a_0 \sin \theta_{C=C_{sthydrin}} 2sp^3 HO}{b} = \sin^{-1} \frac{0.85252a_0 \sin 50.16^{\circ}}{b}$$
 (14.263)

with the use of Eq. (14.261). Substitution of Eq. (14.258) into Eq. (14.263) gives

$$\theta_{C=C_{ethylors},H_2MO} = 60.70^{\circ} \tag{14.264}$$

Then, the distance  $d_{C=C_{ethphas},H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C=C_{ethylens}, H_2MO} = a\cos\theta_{C=C_{ethylens}, H_2MO}$$
(14.265)

Substitution of Eqs. (14.254) and (14.264) into Eq. (14.265) gives

$$d_{C=C_{ethylene}, H_2MO} = 0.72040a_0 = 3.81221 \ X \ 10^{-11} \ m \tag{14.266}$$

The distance  $d_{C=C_{cholens}2sp^3HO}$  along the internuclear axis from the origin of the C atom to the 5 point of intersection of the orbitals is given by

$$d_{C=C_{ellorine} 2sp^3 HO} = c' - d_{C=C_{ellorine}, H_2 MO}$$
(14.267)

Substitution of Eqs. (14.255) and (14.266) into Eq. (14.267) gives

$$d_{C=C_{cholors}2sp^3HO} = 0.54620a_0 = 2.89038 X 10^{-11} m$$
 (14.268)

# 10 FORCE BALANCE OF THE $\it CH_2$ MOs OF ETHYLENE

Each of the two equivalent  $CH_2$  MOs must comprise two C-H bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO as given by Eq. (13.494):

$$2[1 C2sp^3 + 0.75 H_2 MO] \rightarrow CH_2 MO$$
 (14.269)

15

The force balance of the  $CH_2$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.494) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each  $H_2$ -type-20 ellipsoidal-MO component of the  $CH_2$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each C-H-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for 25 the solution of the other axes of each prolate spheroid and eccentricity of each C-H-bond MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_2$  MO are solved.

Consider the formation of the double C = C-bond MO of ethylene from two  $CH_2$  radicals, each having a  $C2sp^3$  shell with an energy given by Eq. (14.146). The energy

components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  are the same as those of the dihydrogen carbide radical, two times those of CH corresponding to the two C-H bonds, except that two times  $E_T(C=C,2sp^3)$  is subtracted from  $E_T(CH_2)$  of Eq. (13.495). The subtraction of the energy change of the  $C2sp^3$  shells with the formation of the C=C-bond MO matches the energy of the C-H-bond MOs to the decrease in the energy of the  $C2sp^3$  HOs. Using Eqs. (13.495) and (14.247),  $E_{T_{charge}}(CH_2)$  is given by

$$E_{T_{chibitan}}(CH_2) = E_T + E(C, 2sp^3) - 2E_T(C = C, 2sp^3)$$

$$= \left(-\frac{2e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] -14.63489 \ eV - \left( -2.26758 \ eV \right)$$
(14.270)

 $E_{T_{culpture}}$  ( $CH_2$ ) given by Eq. (14.270) is set equal to two times the energy of the  $H_2$ -type ellipsoidal MO minus the Coulombic energy of H given by Eq. (13.496):

10 
$$E_{T_{c,t_{0},t_{min}}}(CH_{2}) = \left(-\frac{2e^{2}}{8\pi\varepsilon_{0}c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\right) = -49.66493 \ eV$$

$$(14.271)$$

From the energy relationship given by Eq. (14.271) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_2$  MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.271) gives

15 
$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[ (0.91771)\left(2 - \frac{1}{2}\frac{a_0}{a}\right) \ln\frac{a + \sqrt{\frac{2aa_0}{3}}}{a - \sqrt{\frac{2aa_0}{3}}} - 1\right] = e37.29762$$
 (14.272)

The most convenient way to solve Eq. (14.272) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.56946a_0 = 8.30521 \ X \ 10^{-11} \ m \tag{14.273}$$

Substitution of Eq. (14.273) into Eq. (13.60) gives

$$20 c' = 1.02289a_0 = 5.41290 X 10^{-11} m (14.274)$$

The internuclear distance given by multiplying Eq. (14.274) by two is

$$2c' = 2.04578a_0 = 1.08258 X 10^{-10} m ag{14.275}$$

The experimental bond distance is [3]

$$2c' = 1.087 \times 10^{-10} m \tag{14.276}$$

Substitution of Eqs. (14.273-14.274) into Eq. (14.62) gives

$$b = c = 1.19033a_0 = 6.29897 \ X \ 10^{-11} \ m \tag{14.277}$$

Substitution of Eqs. (14.273-14.274) into Eq. (14.63) gives

$$5 e = 0.65175 (14.278)$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{ellylene} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{elhylene2sp^3} = 0.85252a_0$  is the radius of the  $C_{etlhylene} 2sp^3$  shell. Substitution of Eqs. (14.273-14.274) into Eq. (13.261) gives

$$\theta' = 84.81^{\circ}$$
 (14.279)

Then, the angle  $\theta_{C-H_{ellplene}2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

15 
$$\theta_{C-H_{\text{niprior}} 2sp^3HO} = 180^{\circ} - 84.81^{\circ} = 95.19^{\circ}$$
 (14.280)

as shown in Figure 41.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{elbylene},H_2MO}$  between the 20 internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{elbylene} 2sp^3$  radial vector obeys the following relationship:

$$r_{ethylene2sp^3} \sin \theta_{C-H_{ethylene}2sp^3HO} = 0.85252a_0 \sin \theta_{C-H_{ethylene}2sp^3HO} = b \sin \theta_{C-H,H_2MO}$$
 (14.281)

such that

$$\theta_{C-H_{edylam},H_2MO} = \sin^{-1} \frac{0.85252a_0 \sin \theta_{C-H_{edylam}2sp^3HO}}{h} = \sin^{-1} \frac{0.85252a_0 \sin 95.19^{\circ}}{h}$$
 (14.282)

25 with the use of Eq. (14.280). Substitution of Eq. (14.277) into Eq. (14.282) gives

$$\theta_{C-H_{edinters}, H_2MO} = 45.50^{\circ}$$
 (14.283)

Then, the distance  $d_{C-H_{ethylow},H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{ethylene}, H_2MO} = a\cos\theta_{C-H_{ethylene}, H_2MO} \tag{14.284}$$

Substitution of Eqs. (14.273) and (14.283) into Eq. (14.284) gives

$$d_{C-H_{cthylene},H_2MO} = 1.10002a_0 = 5.82107 \ X \ 10^{-11} \ m \tag{14.285}$$

The distance  $d_{C-H_{chylens} 2sp^3HO}$  along the internuclear axis from the origin of the C atom to the 5 point of intersection of the orbitals is given by

$$d_{C-H_{chylene} 2sp^3HO} = d_{C-H_{chylene}, H_2MO} - c'$$
 (14.286)

Substitution of Eqs. (14.274) and (14.285) into Eq. (14.286) gives

$$d_{C-H_{\text{solution}} 2sp^3HO} = 0.07713a_0 = 4.08171 \ X \ 10^{-12} \ m \tag{14.287}$$

## 10 BOND ANGLE OF THE CH, GROUPS

Each  $CH_2$  MO comprises a linear combination of two C-H-bond MOs. Each C-H-bond MO comprises the superposition of a  $H_2$ -type ellipsoidal MO and the  $C_{ethylene}2sp^3$  HO. A bond is also possible between the two H atoms of the C-H bonds. Such H-H bonding would decrease the C-H bond strength since electron density would be shifted from the 15 C-H bonds to the H-H bond. Thus, the bond angle between the two C-H bonds is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal H atoms of the C-H bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the H-H ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{14.288}$$

20 The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.289}$$

The length of the semiminor axis of the prolate spheroidal H-H MO b=c is given by Eq. (14.62).

The bond angle of the  $CH_2$  groups of ethane is derived by using the orbital composition and an energy matching factor as in the case with the dihydrogen carbide radical and the  $CH_3$  groups of ethane. Since the two  $H_2$ -type ellipsoidal MOs initially comprise 75% of the H electron density of  $H_2$  and the energy of each  $H_2$ -type ellipsoidal MO is matched to that of the  $C_{ellplene} 2sp^3$  HO, the component energies and the total energy  $E_T$  of the

H-H bond are given by Eqs. (13.67-13.73) except that  $V_{\sigma}$ , T, and  $V_{m}$  are corrected for the hybridization-energy-matching factor of 0.85252. Hybridization with 25% electron donation to the C=C-bond gives rise to the  $C_{ethylene}2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$  given by Eq. (14.245). The corresponding normalization factor for determining the zero of the total H-H bond energy is given by the ratio of 15.95955 eV, the magnitude of  $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$  given by Eq. (14.245), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The hybridization energy factor  $C_{ethyleneC2sp^3HO}$  is

$$C_{ethyleneC2:p^3HO} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{ethylene2:p^3}}} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.85252a_0}} = \frac{13.605804 \ eV}{15.95955 \ eV} = 0.85252 \quad (14.290)$$

Substitution of Eq. (14.290) into Eq. (13.233) or Eq. (14.195) with the hybridization factor of 0.85252 gives

of 0.85252 gives
$$0 = \begin{bmatrix} \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left[ (0.85252)^{-1} \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_o a^3}}}{\frac{m_e}{m_e c^2}}} \right] + \hbar\sqrt{\frac{0.75e^2}{8\pi\varepsilon_o a^3} \frac{e^2}{8\pi\varepsilon_o (a + c')^3}}{0.5m_p}}$$
(14.291)

From the energy relationship given by Eq. (14.291) and the relationship between the axes given by Eqs. (14.192-14.193) and (14.62-14.63), the dimensions of the H-H MO can be solved.

The most convenient way to solve Eq. (14.291) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 6.0400a_0 = 3.1962 X 10^{-10} m ag{14.292}$$

20 Substitution of Eq. (14.292) into Eq. (14.288) gives

$$c' = 1.7378a_0 = 9.1961 \ X \ 10^{-11} \ m \tag{14.293}$$

The internuclear distance given by multiplying Eq. (14.293) by two is

$$2c' = 3.4756a_0 = 1.8392 \ X \ 10^{-10} \ m \tag{14.294}$$

Substitution of Eqs. (14.292-14.293) into Eq. (14.62) gives

$$b = c = 5.7846a_0 = 3.0611 \ X \ 10^{-10} \ m \tag{14.295}$$

Substitution of Eqs. (14.292-14.293) into Eq. (14.63) gives

$$5 e = 0.2877 (14.296)$$

From,  $2c'_{H-H}$  (Eq. (14.294)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (14.291)), and  $2c'_{C-H}$  (Eq. (14.275)), the internuclear distance of each C-H bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle  $\theta_{HCH}$  between the C-H bonds

10 is

$$\theta_{HCH} = \cos^{-1}\left(\frac{2(2.04578)^2 - (3.4756)^2}{2(2.04578)^2}\right) = \cos^{-1}(-0.44318) = 116.31^{\circ}$$
 (14.297)

The experimental angle between the C-H bonds is [11]

$$\theta_{HCH} = 116.6^{\circ} \tag{14.298}$$

The C=C bond is along the z-axis. Thus, based on the symmetry of the equivalent bonds, 15 the bond angle  $\theta_{C=C-H}$  between the internuclear axis of the C=C bond and a H atom of the  $CH_2$  groups is given by

$$\theta_{C=C-H} = \frac{(360^{\circ} - \theta_{CHC})}{2} \tag{14.299}$$

Substitution of Eq. (14.298) into Eq. (14.299) gives

$$\theta_{C+C-H} = 121.85^{\circ} \tag{14.300}$$

20 The experimental angle between the C = C - H bonds is [11]

$$\theta_{C=C-H} = 121.7^{\circ}$$
 (14.301)

and [3]

$$\theta_{C=C-H} = 121.3^{\circ} \tag{14.302}$$

The C=C bond and H atoms of ethylene line in a plane, and rotation about the C=C is not possible due to conservation of angular momentum in the two sets of spin-paired electrons of the double bond. The  $CH_2CH_2$  MO shown in Figure 42 was rendered using these parameters.

The charge-density in the C = C-bond MO is increased by a factor of 0.25 per bond with the formation of the  $C_{ellustere} 2sp^3$  HOs each having a smaller radius. Using the orbital

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composition of the  $CH_2$  groups (Eq. (14.269)) and the C=C-bond MO (Eq. (14.242), the radii of  $C1s=0.17113a_0$  (Eq. (10.51)) and  $C_{ethylene}2sp^3=0.85252a_0$  (Eq. (14.244)) shells, and the parameters of the C=C-bond (Eqs. (13.3-13.4), (14.254-14.256), and (14.258-14.268)), the parameters of the C-H-bond MOs (Eqs. (13.3-13.4), (14.273-14.275), and (14.277-14.287)), and the bond-angle parameters (Eqs. (14.297-14.302)), the charge-density of the  $CH_2CH_2$  MO comprising the linear combination of two sets of two C-H-bond MOs and a C=C-bond MO bridging the two  $CH_2$  groups is shown in Figure 42. Each C-H-bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C_{ethylene}2sp^3$  HO having the dimensional diagram shown in Figure 41. The C=C-bond MO comprises a  $H_2$ -type ellipsoidal MO bridging two  $C_{ethylene}2sp^3$  HOs having the dimensional diagram shown in Figure 40.

## ENERGIES OF THE CH<sub>2</sub> GROUPS

The energies of each  $CH_2$  group of ethylene are given by the substitution of the semiprincipal axes (Eqs. (14.273-14.274) and (14.277)) into the energy equations of dihydrogen carbide 15 (Eqs. (13.510-13.514)), with the exception that two times  $E_T(C=C,2sp^3)$  (Eq. (14.247)) is subtracted from  $E_T(CH_2)$  in Eq. (13.514):

$$V_e = 2(0.91771) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -76.00757 \ eV$$
 (14.303)

$$V_p = \frac{2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 26.60266 \ eV \tag{14.304}$$

$$T = 2(0.91771) \frac{\hbar^2}{2m \cdot a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 24.21459 \ eV$$
 (14.305)

20 
$$V_m = 2(0.91771) \frac{-\hbar^2}{4m_a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -12.10730 \text{ eV}$$
 (14.306)

$$E_{T_{ethylene}}(CH_2) = \left(-\frac{2e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \right) = -49.66493 \ eV$$
(14.307)

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where  $E_{T_{ethylens}}$  (CH<sub>2</sub>) is given by Eq. (14.270) which is reiteratively matched to Eq. (13.496) within five-significant-figure round off error.

### VIBRATION OF THE 12CH, GROUPS

5 The vibrational energy levels of  $CH_2$  in ethylene may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

10

#### THE DOPPLER ENERGY TERMS OF THE 12CH2 GROUPS

The equations of the radiation reaction force of the  $CH_2$  groups in ethylene are the same as those of the dihydrogen carbide radical with the substitution of the  $CH_2$ -group parameters. Using Eq. (13.515), the angular frequency of the reentrant oscillation in the transition state is

15 
$$\omega = \sqrt{\frac{0.75e^2}{\frac{4\pi\varepsilon_0 b^3}{m_e}}} = 2.75685 \, X \, 10^{16} \, rad/s$$
 (14.308)

where b is given by Eq. (14.277). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_{\kappa} = \hbar \omega = \hbar 2.75685 \, X \, 10^{16} \, rad/s = 18.14605 \, eV$$
 (14.309)

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total 20 energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.309) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(18.14605 \ eV)}{m_e c^2}} = -0.26660 \ eV \tag{14.310}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the 25 transition state at their corresponding frequency. The decrease in the energy of  $CH_2$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{asc}$ , is given by the sum of the corresponding

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energies,  $\overline{E}_D$  given by Eq. (14.310) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each C-H bond. Using  $\omega_e$  given by Eq. (13.458) for  $\overline{E}_{Kvib}$  of the transition state having two independent bonds,  $\overline{E}_{ethylene\ osc}^{\ \ \ \ \ \ \ \ \ \ \ \ \ \ }$  per bond is

$$\overline{E}'_{ethylene\ osc}\left(^{12}CH_{2}\right) = \overline{E}_{D} + \overline{E}_{Kvib} = \overline{E}_{D} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
 (14.311)

5 
$$\overline{E}'_{\text{ethylene osc}} \left(^{12}CH_2\right) = -0.26660 \ eV + \frac{1}{2} \left(0.35532 \ eV\right) = -0.08894 \ eV$$
 (14.312)

Given that the vibration and reentrant oscillation is for two C-H bonds,  $\overline{E}_{ethylene\ osc}\left(^{12}CH_{2}\right)$ , is:

$$\overline{E}_{ethylene \ osc} \left( {}^{12}CH_2 \right) = 2 \left( \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) 
= 2 \left( -0.26660 \ eV + \frac{1}{2} \left( 0.35532 \ eV \right) \right) 
= -0.17788 \ eV$$
(14.313)

### 10 TOTAL AND DIFFERENCE ENERGIES OF THE 12CH, GROUPS

 $E_{ethyleneT+osc}\left(^{12}CH_{2}\right)$ , the total energy of each  $^{12}CH_{2}$  group including the Doppler term, is given by the sum of  $E_{T_{ethylene}}\left(CH_{2}\right)$  (Eq. (14.307)) and  $\overline{E}_{ethylene\,osc}\left(^{12}CH_{2}\right)$  given by Eq. (14.313):

$$E_{ethyleneT+osc}\left(CH_{2}\right) = \begin{pmatrix} V_{e} + T + V_{m} + V_{p} + E\left(C, 2sp^{3}\right) \\ -2E_{T}\left(C = C, 2sp^{3}\right) + \overline{E}_{ethylene\ osc}\left({}^{12}CH_{2}\right) \end{pmatrix}$$

$$= E_{T_{ethylene}}\left(CH_{2}\right) + \overline{E}_{ethylene\ osc}\left({}^{12}CH_{2}\right)$$
(14.314)

$$E_{elipleneT+osc} \begin{pmatrix} \frac{-2e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \\ -14.63489 \, eV - \left( -2.26759 \, eV \right) \end{pmatrix}$$

$$= -49.66493 \, eV - 2 \left( 0.26660 \, eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$

$$= -49.66493 \, eV - 2 \left( 0.26660 \, eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$

$$= -49.66493 \, eV - 2 \left( 0.26660 \, eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$

From Eqs. (14.313-14.315), the total energy of each  $^{12}CH_2$  is

$$\begin{split} E_{ethyleneT+asc}\left(^{12}CH_{2}\right) &= -49.66493 \ eV + \overline{E}_{ethylene \ osc}\left(^{12}CH_{2}\right) \\ &= -49.66493 \ eV - 2\bigg(0.26660 \ eV - \frac{1}{2}\big(0.35532 \ eV\big)\bigg) \\ &= -49.84282 \ eV \end{split} \tag{14.316}$$

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

5

The total energy for each dihydrogen carbide radical given by Eq. (13.523) is

$$E_{radicalT+asc} {1^{2}CH_{2}} = -49.66493 \ eV + \overline{E}_{radicalosc} {1^{2}CH_{2}}$$

$$= -49.66493 \ eV - 2 \left( 0.25493 \ eV - \frac{1}{2} (0.35532 \ eV) \right)$$

$$= -49.81948 \ eV$$
(14.317)

The difference in energy between the  $CH_2$  groups and the dihydrogen carbide radical  $\Delta E_{T+asc}(^{12}CH_2)$  is given by two times the difference between Eqs. (14.316) and (14.317):

$$\Delta E_{T+asc} \left( {}^{12}CH_2 \right) = 2 \left( E_{elhyleneT+osc} \left( {}^{12}CH_2 \right) - E_{radicalT+osc} \left( {}^{12}CH_2 \right) \right)$$

$$= 2 \left( -49.84282 \, eV - \left( -49.81948 \, eV \right) \right)$$

$$= -0.04667 \, eV$$
(14.318)

# 10 SUM OF THE ENERGIES OF THE C=C $\sigma$ MO AND THE HOS OF ETHYLENE

The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of the C=C-bond MO are the same as those of the CH MO except that each term is multiplied by two corresponding to the double bond and the energy term corresponding to the  $C_{ethylene}2sp^3$  HOs in the equation for  $E_T$  is zero. The energies of each C=C-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.254-14.255) and (14.258)) into two times the energy equations of the CH MO (Eqs. (13.449-13.453)), with the exception that zero replaces  $E\left(C,2sp^3\right)$  in Eq. (13.453):

$$V_e = 2(0.91771) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -102.08992 \ eV$$
 (14.319)

20 
$$V_p = 2 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 21.48386 \, eV \tag{14.320}$$

$$T = 2(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 34.67062 \text{ eV}$$
 (14.321)

$$V_m = 2(0.91771) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -17.33531 \ eV$$
 (14.322)

$$E_T(C=C,\sigma) = -\frac{2e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] = -63.27075 \ eV \ (14.323)$$

where  $E_T(C=C,\sigma)$  is the total energy of the C=C  $\sigma$  MO given by Eq. (14.251) which is 5 reiteratively matched to two times Eq. (13.75) within five-significant-figure round off error.

The total energy of the C=C-bond MO,  $E_T(C=C)$ , is given by the sum of two times  $E_T(C=C,2sp^3)$ , the energy change of each  $C2sp^3$  shell due to the decrease in radius with the formation of the C=C-bond MO (Eq. (14.247)), and  $E_T(C=C,\sigma)$ , the  $\sigma$  MO contribution given by Eq. (14.252):

$$E_{T}(C=C) = 2E_{T}(C=C,2sp^{3}) + E_{T}(C=C,\sigma)$$

$$= \begin{pmatrix} 2(-1.13380 \ eV) + \\ \left(-\frac{2e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left(2 - \frac{1}{2} \frac{a_{0}}{a}\right) \ln \frac{a+c'}{a-c'} - 1\right] \right)$$

$$= 2(-1.13380 \ eV) + (-63.27074 \ eV)$$

$$= -65.53833 \ eV$$

$$(14.324)$$

#### VIBRATION OF ETHYLENE

The vibrational energy levels of  $CH_2CH_2$  may be solved as two sets of two equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE C = C-BOND MO OF 20 ETHYLENE

The equations of the radiation reaction force of the C = C-bond MO are given by Eq. (13.142), except the force-constant factor is (0.93172)0.5 based on the force constant k' of

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Eq. (14.248), and the C = C-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.91771 \frac{(0.5)e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 4.30680 \, X \, 10^{16} \, rad/s \tag{14.325}$$

where b is given by Eq. (14.258). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. 5 (11.127)):

$$\bar{E}_K = \hbar \omega = \hbar 4.30680 \, X \, 10^{16} \, rad/s = 28.34813 \, eV$$
 (14.326)

In Eq. (11.181), substitution of  $E_T(C=C)/2$  (Eq. (14.324)) for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.326) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

10 
$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -32.76916 \ eV \sqrt{\frac{2e(28.34813 \ eV)}{m_e c^2}} = -0.34517 \ eV$$
 (14.327)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the C = C-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (14.327) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of the C = C bond. Using the experimental C = C  $E_{vib}(v_3)$  of 1443.5  $cm^{-1}(0.17897 \ eV)$  [12] for  $\overline{E}_{Kvib}$  of the transition state having two bonds,  $\overline{E}'_{osc}(C = C, \sigma)$  per bond is

$$\overline{E}'_{osc}(C=C,\sigma) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(14.328)

20 
$$\bar{E}'_{osc}(C=C,\sigma) = -0.34517 \, eV + \frac{1}{2}(0.17897 \, eV) = -0.25568 \, eV$$
 (14.329)

Given that the vibration and reentrant oscillation is for two C-C bonds of the C=C double bond,  $\overline{E}_{ethylene\ osc}\left(C=C,\sigma\right)$ , is:

$$\overline{E}_{ethylene \ osc} \left( C = C, \sigma \right) = 2 \left( \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) = 2 \left( -0.34517 \ eV + \frac{1}{2} \left( 0.17897 \ eV \right) \right) = -0.51136 \ eV$$
(14.330)

## TOTAL ENERGIES OF THE C = C-BOND MO OF ETHYLENE

 $E_{T+osc}\left(C=C\right)$ , the total energy of the C=C-bond MO including the Doppler term, is given by the sum of  $E_{T}\left(C=C\right)$  (Eq. (14.324)) and  $\overline{E}_{elhylene\ asc}\left(C=C,\sigma\right)$  given by Eq. (14.330):

$$E_{T+asc}\left(C=C\right) = V_{e} + T + V_{m} + V_{p} + 2E_{T}\left(C=C, 2sp^{3}\right) + \overline{E}_{ethylene\ osc}\left(C=C, \sigma\right)$$

$$= E_{T}\left(C=C, \sigma\right) + 2E_{T}\left(C=C, 2sp^{3}\right) + \overline{E}_{ethylene\ osc}\left(C=C, \sigma\right)$$

$$= E_{T}\left(C=C\right) + \overline{E}_{ethylene\ osc}\left(C=C, \sigma\right)$$
(14.331)

$$E_{T+osc}(C=C) = \begin{cases} \left(\frac{-2e^{2}}{8\pi\varepsilon_{0}c^{1}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_{0}}{a}\right)\ln\frac{a+c^{1}}{a-c^{1}}-1\right] + 2E_{T}\left(C=C,2sp^{3}\right)\right) \\ \left(1+\left(2\right)\left(\frac{1}{2}\right)\sqrt{\frac{2\hbar\sqrt{\frac{(0.91771)\frac{1}{2}\frac{e^{2}}{4\pi\varepsilon_{0}b^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right) + 2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{cases}$$

$$= -65.53833 \ eV - 2\left(0.34517 \ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$(14.332)$$

From Eqs. (14.330-14.332), the total energy of the C = C-bond MO is

$$E_{T+asc}(C=C) = -63.27074 \ eV + 2E_{T}(C=C,2sp^{3}) + \overline{E}_{ethylene \ osc}(C=C,\sigma)$$

$$= -63.27074 \ eV + 2(-1.13380 \ eV) - 2\left(0.34517 \ eV - \frac{1}{2}(0.17897 \ eV)\right)$$

$$= -66.04969 \ eV$$
(14.333)

where the experimental  $E_{vib}$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

10

## BOND ENERGY OF THE C = C BOND OF ETHYLENE

The dissociation energy of the C=C bond of  $CH_2CH_2$ ,  $E_D\left(H_2C=CH_2\right)$ , is given by four times  $E\left(C,2sp^3\right)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each  $CH_2$  radical that forms the double C=C bond, minus the sum of  $\Delta E_{T+osc}\left(^{12}CH_2\right)$  (Eq. (14.318)), the energy change going from the dihydrogen carbide radicals to the  $CH_2$  groups of ethylene, and  $E_{T+osc}\left(C=C\right)$  (Eq. (14.333)). Thus, the dissociation energy of the C=C bond of  $CH_2CH_2$ , is

$$E_{D}(H_{2}C = CH_{2}) = 4(E(C, 2sp^{3})) - (\Delta E_{T+asc}(^{12}CH_{2}) + E_{T+asc}(C = C))$$

$$= 4(-14.63489 eV) - (-0.04667 eV - 66.04969 eV)$$

$$= 4(-14.63489 eV) - (-66.09636 eV)$$

$$= 7.55681 eV$$
(14.334)

The experimental dissociation energy of the C = C bond of  $CH_2CH_2$  is [7]

$$E_D(H_2C - CH_2) = 7.5969 \text{ eV}$$
 (14.335)

The results of the determination of bond parameters of  $CH_2CH_2$  are given in Table 5 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

#### ACETYLENE MOLECULE (CHCH)

10 The acetylene molecule CHCH is formed by the reaction of two hydrogen carbide radicals:

$$CH + CH \rightarrow CHCH \tag{14.336}$$

CHCH can be solved using the same principles as those used to solve the methane series CH<sub>n=1,2,3,4</sub> as well as ethane, wherein the 2s and 2p shells of each C hybridize to form a single 2sp³ shell as an energy minimum, and the sharing of electrons between two C2sp³ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of one H atomic orbital (AO) combine with two sets of one carbon 2sp³ HO to form two hydrogen carbide groups comprising a linear combination of two diatomic H₂-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two
CH groups bond by forming a H₂-type MO between the remaining three C2sp³ HOs on each carbon atom.

#### FORCE BALANCE OF THE C = C-BOND MO OF ACETYLENE

CHCH comprises a chemical bond between two CH radicals wherein each radical comprises a chemical bond between a carbon and a hydrogen atom. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. The C-H bond of CH having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75%  $H_2$ -type

ellipsoidal MO and 25%  $C2sp^3$  HO. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , the C-H-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at the H proton that is continuous with the  $C2sp^3$  shell at the C atom whose nucleus serves as the other focus. The electron configuration and the energy,  $E(C,2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of the C-H bond is provided by the spin-pairing force of the CH MO that has the symmetry of an s orbital that superimposes with the  $C2sp^3$  orbitals such that the corresponding angular momenta are unchanged.

Two CH radicals bond to form CHCH by forming a MO between the two pairs of three remaining  $C2sp^3$ -HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between two  $C2sp^3$  HOs to form a MO comprising six spin-paired electrons permits each  $C2sp^3$  HO to decrease in radius and energy.

As in the case of the C-H bonds, the  $C \equiv C$ -bond MO is a prolate-spheroidal-MO surface that cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the  $C2sp^3$  shell at each C atom. The energy of the  $H_2$ -20 type ellipsoidal MO is matched to that of the  $C2sp^3$  shell. As in the case of previous examples of energy-matched MOs such as those of OH, NH, CH, the C = O-bond MO of  $CO_2$ , the C-C-bond MO of  $CH_3CH_3$ , and the C = C-bond MO of  $CH_2CH_2$ , the  $C \equiv C$ -bond MO of acetylene must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the  $C \equiv C$ -bond MO must comprise 25 a linear combination of three MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$3(2C2sp^3 + 0.75 H_2 MO) \rightarrow C \equiv C - bond MO$$
 (14.337)

The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution from each  $C2sp^3$  HO to the  $C \equiv C$ -bond MO to achieve an energy minimum. The force balance of the  $C \equiv C$ -bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.337) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

Similarly, the energies of each CH MO involve each  $C2sp^3$  and each H1s electron with the formation of each C-H bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. This energy is determined by the considering the effect of the donation of 25% electron density from the three pairs of  $C2sp^3$  HOs to the  $C \equiv C$ -bond MO with the formation of the  $C_{acetylene}2sp^3$  HOs each having a smaller radius. The  $2sp^3$  hybridized orbital arrangement is given by Eq. (14.140). The sum  $E_T(C,2sp^3)$  of calculated energies of C,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.141). The radius  $r_{2sp^3}$  of the  $C2sp^3$  shell is given by Eq. (14.142). The Coulombic energy  $E_{Coulomb}(C,2sp^3)$  and the energy  $E(C,2sp^3)$  of the outer electron of the  $C2sp^3$  shell are given by Eqs. (14.143) and (14.146), respectively.

Next, consider the formation of the  $C \equiv C$ -bond MO of acetylene from two CH radicals, each having a  $C2sp^3$  electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum  $E_T(C_{acetylene}, 2sp^3)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$E_T(C_{acesylene}, 2sp^3) = -(64.3921 eV + 48.3125 eV + 24.2762 eV + E(C, 2sp^3))$$

$$= -(64.3921 eV + 48.3125 eV + 24.2762 eV + 14.63489 eV)$$

$$= -151.61569 eV$$

(14.338)

where  $E(C,2sp^3)$  (Eq. (14.146)) is the sum of the energy of C,  $-11.27671\,eV$ , and the 25 hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the  $E_T(C_{acetylene},2sp^3)$  is purely Coulombic.

The sharing of electrons between three pairs of  $C2sp^3$  HOs to form a  $C \equiv C$ -bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating  $C2sp^3$  HO donates an excess of 25% of its electron density to the  $C \equiv C$ -bond MO to form an energy minimum. By considering this electron redistribution in the acetylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{acetylene2sp^3}$  of the  $C2sp^3$  shell of acetylene may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{acetylene2sp^3} = \left(\sum_{n=2}^{5} (Z-n) - 0.75\right) \frac{e^2}{8\pi\varepsilon_0 \left(e151.61569 \, eV\right)}$$

$$= \frac{9.25e^2}{8\pi\varepsilon_0 \left(e151.61569 \, eV\right)}$$

$$= 0.83008a_0$$
(14.339)

10 where Z=6 for carbon. Using Eqs. (10.102) and (14.339), the Coulombic energy  $E_{Coulomb}\left(C_{acetylene},2sp^3\right)$  of the outer electron of the  $C2sp^3$  shell is

$$E_{Coulomb}\left(C_{acetylene}, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{acetylene2sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.83008a_{0}} = -16.39089 \ eV \qquad (14.340)$$

During hybridization, one of the spin-paired 2s electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. 15 (13.152). Using Eqs. (14.145) and (14.340), the energy  $E(C_{acetylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E\left(C_{acetylene}, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{acetylene2sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}} = -16.39089 \ eV + 0.19086 \ eV = -16.20002 \ eV$$

(14.341)

20 Thus,  $E_T(C \equiv C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of the  $C \equiv C$ -bond MO is given by the difference between Eq. (14.146) and Eq. (14.341):

$$E_{T}(C \equiv C, 2sp^{3}) = E(C_{acetylens}, 2sp^{3}) - E(C, 2sp^{3})$$

$$= -16.20002 \ eV - (-14.63489 \ eV)$$

$$= -1.56513 \ eV$$
(14.342)

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As in the case of  $Cl_2$ , each  $H_2$ -type ellipsoidal MO comprises 75% of the  $C \equiv C$ -bond MO shared between two  $C2sp^3$  HOs corresponding to the electron charge density in Eq. (11.65) of  $\frac{-0.75e}{2}$ . But, the additional 25% charge-density contribution to each bond of the  $C \equiv C$ -bond MO causes the electron charge density in Eq. (11.65) to be is given by  $\frac{-e}{2} = -0.5e$ . The 5 corresponding force constant  $k^1$  to determine the ellipsoidal parameter  $e^1$  in terms of the central force of the foci (Eq. (11.65)) is given by Eq. (14.152). The distance from the origin to each focus  $e^1$  is given by Eq. (14.153). The internuclear distance is given by Eq. (14.154). The length of the semiminor axis of the prolate spheroidal  $C \equiv C$ -bond MO  $e^1$  is given by Eq. (13.62). The eccentricity,  $e^1$ , is given by Eq. (13.63). The solution of the semimajor axis 10  $e^1$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of the  $e^1$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of the  $e^1$  then allows for the solution of the energy equation and the relationship between the axes, the dimensions of the  $e^1$  bench MO are solved.

The general equations for the energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of the C = C-bond MO are the same as those of the CH MO except that energy of the  $C_{acetMene} 2sp^3$ 15 HO is used and the triple-bond nature is considered. In the case of a single bond, the prolate spheroidal  $H_2$ -type MO transitions to the  $C_{acetylene} 2sp^3$  HO of each carbon, and the energy of the  $C_{acetylene}2sp^3$  shell must remain constant and equal to the  $E\left(C_{acetylene},2sp^3\right)$  given by Eq. (14.391). Thus, the energy  $E(C_{acetylene}, 2sp^3)$  in Eq. (14.391) adds to that of the energies of the corresponding  $H_2$ -type ellipsoidal MO. The second and third bonds of the triple C = C-20 bond MO also transition to each  $C_{acetylene} 2sp^3$  HO of each C. The energy of a second and a third  $H_2$ -type ellipsoidal MO adds to the first energy component, and the three bonds achieve an energy minimum as a linear combination of the three  $H_2$ -type ellipsoidal MOs each having the carbon nuclei as the foci. Each C-C-bond MO comprises the same  $C_{acetylene}2sp^3$ HO shells of constant energy given by Eq. (14.391). As in the case of the water,  $NH_2$ , 25 ammonia, and ethylene molecules given by Eqs. (13.180), (13.320), (13.372), and (14.251), respectively, the energy of the redundant shell is subtracted from the total energy of the linear combination of the  $\sigma$  MO. Thus, the total energy  $E_T(C \equiv C, \sigma)$  of the  $\sigma$  component of the  $C \equiv C$ -bond MO is given by the sum of the energies of the three bonds each comprising the

linear combination of the  $C_{acetylene}2sp^3$  HO and the  $H_2$ -type ellipsoidal MO as given by Eq. (14.337) wherein the  $E_T$  terms add positively and the  $E\left(C_{acetylene},2sp^3\right)$  term is positive due to the sum over a negative and two positive terms. Using Eqs. (13.431) and (14.341),  $E_T\left(C\equiv C,\sigma\right)$  is given by

$$E_{T}(C \equiv C, \sigma) = E_{T} + E(C_{acetylene}, 2sp^{3}) - E(C_{acetylene}, 2sp^{3}) - E(C_{acetylene}, 2sp^{3})$$

$$= -\frac{3e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - E(C_{acetylene}, 2sp^{3})$$

$$= -\frac{3e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + 16.20002 \ eV$$

$$(14.343)$$

The total energy term of the double  $C \equiv C$ -bond MO is given by the sum of the three  $H_2$ -type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition,  $E_T(C \equiv C, \sigma)$  given by Eq. (14.343) is set equal to three times Eq. (13.75):

10 
$$E_r(C \equiv C, \sigma) = -\frac{3e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + 16.20002 \ eV = -94.90610 \ eV$$
 (14.344)

From the energy relationship given by Eq. (14.344) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the  $C \equiv C$ -bond MO can be solved.

15 Substitution of Eq. (14.153) into Eq. (14.344) gives

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{aa_0}} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{aa_0}}{a - \sqrt{aa_0}} - 1 \right] = e111.10613$$
 (14.345)

The most convenient way to solve Eq. (14.345) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.28714a_0 = 6.81122 X 10^{-11} m ag{14.346}$$

20 Substitution of Eq. (14.346) into Eq. (14.153) gives

$$c' = 1.13452a_0 = 6.00362 X 10^{-11} m ag{14.347}$$

The internuclear distance given by multiplying Eq. (14.347) by two is

$$2c' = 2.26904a_0 = 1.20072 X 10^{-10} m (14.348)$$

The experimental bond distance is [3]

$$25 2c' = 1.203 X 10^{-10} m (14.349)$$

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Substitution of Eqs. (14.346-14.347) into Eq. (13.62) gives

$$b = c = 0.60793a_0 = 3.21704 X 10^{-11} m ag{14.350}$$

Substitution of Eqs. (14.346-14.347) into Eq. (13.63) gives

$$e = 0.88143 \tag{14.351}$$

5 The nucleus of the C atoms comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{acetylene}2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{acetylene2sp^3} = 0.83008a_0$  is the radius of the  $C_{acetylene}2sp^3$  shell. Substitution of Eqs. (14.346-14.347) into Eq. (13.261) gives

10 
$$\theta' = 137.91^{\circ}$$
 (14.352)

Then, the angle  $\theta_{C=C_{acceptors}2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C=C_{accoden} 2sp^3HO} = 180^{\circ} - 137.91^{\circ} = 42.09^{\circ}$$
 (14.353)

as shown in Figure 43.

15

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C=C_{acayless},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with each  $C_{aceyless}2sp^3$  radial vector obeys the following 20 relationship:

$$r_{acetylene2sp^3}\sin\theta_{C=C_{ocetylene}2sp^3HO} = 0.83008a_0\sin\theta_{C=C_{acetylene}2sp^3HO} = b\sin\theta_{C=C_{acetylene},H_2MO}$$
 (14.354)

such that

$$\theta_{C = C_{accrylens}, H_2MO} = \sin^{-1} \frac{0.83008a_0 \sin \theta_{C = C_{accrylens} 2.sp^3 HO}}{b} = \sin^{-1} \frac{0.83008a_0 \sin 42.09^{\circ}}{b} (14.355)$$

with the use of Eq. (14.353). Substitution of Eq. (14.350) into Eq. (14.355) gives

$$\theta_{C=C_{ocenteus}, H_2MO} = 66.24^{\circ} \tag{14.356}$$

Then, the distance  $d_{C = C_{centrus}, H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C=C_{constant},H,MO} = a\cos\theta_{C=C_{constant},H,MO}$$
 (14.357)

Substitution of Eqs. (14.346) and (14.356) into Eq. (14.357) gives

$$d_{C=C_{certham}, H_2MO} = 0.51853a_0 = 2.74396 X 10^{-11} m$$
 (14.358)

The distance  $d_{C=C_{accptes},2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C = C_{\text{constant}} 250^3 HO} = c' - d_{C = C_{\text{acceptors}}, H_2 MO}$$

$$(14.359)$$

5 Substitution of Eqs. (14.347) and (14.358) into Eq. (14.359) gives

$$d_{C=C_{\text{coord-large}}2sp^3HO} = 0.61599a_0 = 3.25966 X 10^{-11} m$$
 (14.360)

#### FORCE BALANCE OF THE CH MOs OF ACETYLENE

The C-H bond of each of the two equivalent CH MOs must comprise 75% of a  $H_2$ -type 10 ellipsoidal MO and a  $C2sp^3$  HO as given by Eq. (13.429):

$$1 C2sp^3 + 0.75 H_2 MO \rightarrow CH MO$$
 (14.361)

The force balance of the CH MO is determined by the boundary conditions that arise from 15 the linear combination of orbitals according to Eq. (13.429) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each  $H_2$ -type-ellipsoidal-MO component of the CH MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each C-H-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each C-H-bond MO. From the energy equation and the relationship between the axes, the dimensions of the 25 CH MO are solved.

Consider the formation of the triple  $C \equiv C$ -bond MO of acetylene from two CH radicals, each having a  $C2sp^3$  shell with an energy given by Eq. (14.146). The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  are the same as those of the hydrogen carbide radical, except that two times  $E_T(C \equiv C, 2sp^3)$  is subtracted from  $E_T(CH)$  of Eq. (13.495). The 30 subtraction of the energy change of the  $C2sp^3$  shells with the formation of the  $C \equiv C$ -bond

MO matches the energy of the C-H-bond MOs to the decrease in the energy of the  $C2sp^3$  HOs. Using Eqs. (13.495) and (14.342),  $E_{T_{contra}}$  (CH) is given by

$$E_{T_{accrytum}}(CH) = E_T + E(C, 2sp^3) - 2E_T(C = C, 2sp^3)$$

$$= \begin{pmatrix} -\frac{e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \\ -14.63489 \ eV - \left( -3.13026 \ eV \right) \end{pmatrix}$$
(14.362)

 $E_{T_{acceptans}}$  (CH) given by Eq. (14.362) is set equal to the energy of the  $H_2$ -type ellipsoidal MO 5 given by Eq. (13.75):

$$E_{T_{acceptess}}(CH) = \left(-\frac{e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left(2 - \frac{1}{2} \frac{a_0}{a}\right) \ln \frac{a + c'}{a - c'} - 1\right] \right) = -31.63537 \ eV$$

$$-14.63489 \ eV - \left(-3.13026 \ eV\right)$$

(14.363)

From the energy relationship given by Eq. (14.363) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.363) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e20.13074$$
(14.364)

The most convenient way to solve Eq. (14.364) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.48719a_0 = 7.86987 \ X \ 10^{-11} \ m \tag{14.365}$$

15 Substitution of Eq. (14.365) into Eq. (14.60) gives

$$c' = 0.99572a_0 = 5.26913 \ X \ 10^{-11} \ m \tag{14.366}$$

The internuclear distance given by multiplying Eq. (14.366) by two is

$$2c' = 1.99144a_0 = 1.05383 \times 10^{-10} m \tag{14.367}$$

The experimental bond distance is [3]

$$2c' = 1.060 X 10^{-10} m ag{14.368}$$

Substitution of Eqs. (14.365-14.366) into Eq. (14.62) gives

$$b = c = 1.10466a_0 = 5.84561 \ X \ 10^{-11} \ m \tag{14.369}$$

Substitution of Eqs. (14.365-14.366) into Eq. (14.63) gives

$$e = 0.66953 \tag{14.370}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{acesystems} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta^*$  is given by Eq. (13.261) where  $r_n = r_{acctylens} 2sp^3 = 0.83008a_0$  is the radius of the  $C_{acetylens} 2sp^3$  shell. Substitution of Eqs. (14.365-14.366) into Eq. (13.261) gives

$$\theta' = 90.99^{\circ}$$
 (14.371)

Then, the angle  $\theta_{C-H_{accylene}2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

10 
$$\theta_{C-H_{moders}2sp^3HO} = 180^{\circ} - 90.99^{\circ} = 89.01^{\circ}$$
 (14.372)

as shown in Figure 43. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{acoptene},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{aceptene} 2sp^3$  radial vector obeys the following relationship:

15  $r_{acetylene 2sp^3} \sin \theta_{C-H_{acetylene } 2sp^3HO} = 0.83008a_0 \sin \theta_{C-H_{acetylene } 2sp^3HO} = b \sin \theta_{C-H_{acetylene } 1} \sin \theta_{C-H_{acetylene } 1}$  such that

$$\theta_{C-H_{\text{costylens}},H_2MO} = \sin^{-1} \frac{0.83008a_0 \sin \theta_{C-H_{\text{costylens}}2sp^2HO}}{b} = \sin^{-1} \frac{0.83008a_0 \sin 89.01^{\circ}}{b} (14.374)$$

with the use of Eq. (14.372). Substitution of Eq. (14.369) into Eq. (14.374) gives

$$\theta_{C-H_{accryters},H_2MO} = 48.71^{\circ} \tag{14.375}$$

20 Then, the distance  $d_{C-H_{accylene},H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{\text{acctylene}}, H_2MO} = a\cos\theta_{C-H_{\text{acctylene}}, H_2MO} \tag{14.376}$$

Substitution of Eqs. (14.365) and (14.375) into Eq. (14.376) gives

$$d_{C-H_{min},H,MO} = 0.98145a_0 = 5.19359 X 10^{-11} m ag{14.377}$$

25 The distance  $d_{C-H_{conplem}2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{\text{octylene}}2sp^3HO} = c' - d_{C-H_{\text{octylene}},H_2MO}$$
(14.378)

Substitution of Eqs. (14.366) and (14.377) into Eq. (14.378) gives

$$d_{C-H_{accolum}2sp^3HO} = 0.01427a_0 = 7.55329 X 10^{-13} m$$
(14.379)

With the  $C \equiv C$  double bond along one axis, the minimum energy is obtained with the C-H-bond MO at a maximum separation. Thus, the bond angle  $\theta_{C = C-H}$  between the internuclear axis of the  $C \equiv C$  bond and the H atom of the CH groups is

$$\theta_{C=C-H} = 180^{\circ} \tag{14.380}$$

The experimental angle between the  $C \equiv C - H$  bonds is [6]

$$\theta_{C=C-H} = 180^{\circ}$$
 (14.381)

The CHCH MO shown in Figure 44 was rendered using these parameters.

The charge-density in the  $C \equiv C$ -bond MO is increased by a factor of 0.25 per bond with the formation of the  $C_{acetylene}2sp^3$  HOs each having a smaller radius. Using the orbital composition of the CH groups (Eq. (14.361)) and the  $C \equiv C$ -bond MO (Eq. (14.337), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)) and  $C_{acetylene}2sp^3 = 0.83008a_0$  (Eq. (14.339)) shells, and the parameters of the  $C \equiv C$ -bond (Eqs. (13.3-13.4), (14.346-14.348), and (14.350-14.360)), the parameters of the C - H-bond MOs (Eqs. (13.3-13.4), (14.365-14.367), and (14.369-14.379)), and the bond-angle parameter (Eqs. (14.380-14.381)), the charge-density of the CHCH MO comprising the linear combination of two C - H-bond MOs and a  $C \equiv C$ -bond MO bridging the two CH groups is shown in Figure 44. Each C - H-bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C_{acetylene}2sp^3$  HO having the dimensional diagram shown in Figure 43. The  $C \equiv C$ -bond MO comprises a  $H_2$ -type ellipsoidal MO bridging two

#### ENERGIES OF THE CH GROUPS

The energies of each CH group of acetylene are given by the substitution of the semiprincipal axes (Eqs. (14.365-14.366) and (14.369)) into the energy equations of hydrogen 25 carbide (Eqs. (13.510-13.514)), with the exception that two times  $E_T(C \equiv C, 2sp^3)$  (Eq. (14.342)) is subtracted from  $E_T(CH)$  in Eq. (13.514):

$$V_e = (0.91771) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -40.62396 \ eV$$
 (14.382)

$$V_{p} = \frac{e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} = 13.66428 \ eV \tag{14.383}$$

$$T = (0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 13.65796 \text{ eV}$$
 (14.384)

$$V_{m} = (0.91771) \frac{-\hbar^{2}}{4m_{a}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -6.82898 \ eV$$
 (14.385)

$$E_{T_{accolumn}}(CH) = \begin{pmatrix} -\frac{e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \\ -14.63489 \ eV - \left( -3.13026 \ eV \right) \end{pmatrix} = -31.63532 \ eV$$

5 where  $E_{T_{conplex}}$  (CH) is given by Eq. (14.362) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

### VIBRATION OF THE 12CH GROUPS

The vibrational energy levels of CH in acetylene may be solved using the methods given in 10 the Vibration and Rotation of CH section.

#### THE DOPPLER ENERGY TERMS OF THE 12CH GROUPS

The equations of the radiation reaction force of the CH groups in acetylene are the same as those of the hydrogen carbide radical with the substitution of the CH-group parameters.

15 Using Eq. (13.477), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\epsilon_0 b^3}} = 3.08370 \, X \, 10^{16} \, rad/s \tag{14.387}$$

where b is given by Eq. (14.369). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 3.08370 \ X \ 10^{16} \ rad / s = 20.29747 \ eV$$
 (14.388)

20 In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.388) for  $\overline{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(20.29747 \ eV)}{m_e c^2}} = -0.28197 \ eV$$
 (14.389)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding 5 energies,  $\overline{E}_D$  given by Eq. (14.389) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each C-H bond. Using  $\omega_e$  given by Eq. (13.458) for  $\overline{E}_{Kvib}$  of the transition state,  $\overline{E}_{acetylene\ osc}$  (12CH) is

$$\overline{E}_{acetylene\ osc}\left(^{12}CH\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(14.390)

$$\overline{E}_{acetylene\ osc}\left(^{12}CH\right) = -0.28197\ eV + \frac{1}{2}\left(0.35532\ eV\right) = -0.10430\ eV \tag{14.391}$$

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### TOTAL AND DIFFERENCE ENERGIES OF THE 12CH GROUPS

 $E_{acesyleneT+osc}$  (12CH), the total energy of each 12CH group including the Doppler term, is given by the sum of  $E_{T_{occoplene}}$  (CH) (Eq. (14.386)) and  $\bar{E}_{acesylene\ osc}$  (12CH) given by Eq. (14.391):

$$E_{acetyleneT+osc}(CH) = \begin{pmatrix} V_e + T + V_m + V_p + E(C, 2sp^3) \\ -2E_T(C = C, 2sp^3) + \overline{E}_{acetylene\ osc}(^{12}CH) \end{pmatrix}$$

$$= E_{T_{acetylene}}(CH) + \overline{E}_{acetylene\ osc}(^{12}CH)$$
(14.392)

$$E_{acetyleneT+osc} \binom{12CH}{=} \begin{cases} \left(\frac{-e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left(2 - \frac{1}{2} \frac{a_0}{a}\right) \ln \frac{a + c'}{a - c'} - 1\right] \right) \\ -14.63489 \ eV - (-3.13026 \ eV) \end{cases}$$

$$= -31.63537 \ eV - \left(0.28197 \ eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}\right)$$

$$(14.393)$$

From Eqs. (14.391-14.393), the total energy of each  $^{12}CH$  is

$$E_{acctyleneT+osc} {12CH} = -31.63537 \ eV + \overline{E}_{acctylene \ osc} {12CH}$$

$$= -31.63537 \ eV - \left(0.28197 \ eV - \frac{1}{2}(0.35532 \ eV)\right)$$

$$= -31.73967 \ eV$$
(14.394)

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The total energy for each hydrogen carbide radical given by Eq. (13.485) is

$$E_{radicalT+osc}(^{12}CH) = -31.63537 \ eV + \overline{E}_{radicalosc}(^{12}CH)$$

$$= -31.63537 \ eV - 0.24966 \ eV + \frac{1}{2}(0.35532 \ eV)$$

$$= -31.70737 \ eV$$
(14.395)

5 The difference in energy between the *CH* groups and the hydrogen carbide radical  $\Delta E_{T+asc}(^{12}CH)$  is given by two times the difference between Eqs. (14.394) and (14.395):

$$\Delta E_{T+asc} \binom{12}{CH} = 2 \left( E_{acetyleneT+osc} \binom{12}{CH} - E_{radicalT+osc} \binom{12}{CH} \right)$$

$$= 2 \left( -31.73967 \ eV - \left( -31.70737 \ eV \right) \right)$$

$$= -0.06460 \ eV$$
(14.396)

# SUM OF THE ENERGIES OF THE $C \equiv C$ $\sigma$ MO AND THE HOS OF 10 ACETYLENE

The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of the  $C \equiv C$ -bond MO are the same as those of the CH MO except that each term is multiplied by three corresponding to the triple bond and the energy term corresponding to the  $C_{acceptene} 2sp^3$  HOs in the equation for  $E_T$  is positive. The energies of each  $C \equiv C$ -bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.346-14.347) and (14.350)) into three times the energy equations of the CH MO (Eqs. (13.449-13.453)), with the exception that  $E(C, 2sp^3)$  in Eq. (13.453) is positive and given by Eq. (14.341):

$$V_{e} = 3(0.91771) \frac{-2e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} = -182.53826 \ eV$$
 (14.397)

$$V_p = 3 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 35.97770 \ eV \tag{14.398}$$

$$T = 3(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 70.90876 \, eV$$
 (14.399)

$$V_m = 3(0.91771) \frac{-\hbar^2}{4m_a a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -35.45438 \ eV$$
 (14.400)

$$E_{T}(C = C, \sigma) = -\frac{3e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + 16.20002 \ eV = -94.90616 \ eV$$
(14.401)

5 where  $E_T(C \equiv C, \sigma)$  is the total energy of the  $C \equiv C$   $\sigma$  MO given by Eq. (14.343) which is reiteratively matched to three times Eq. (13.75) within five-significant-figure round off error.

The total energy of the  $C \equiv C$ -bond MO,  $E_T(C \equiv C)$ , is given by the sum of two times  $E_T(C \equiv C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell due to the decrease in radius with the formation of the  $C \equiv C$ -bond MO (Eq. (14.342)), and  $E_T(C \equiv C, \sigma)$ , the  $\sigma$  MO tontribution given by Eq. (14.344):

$$E_{T}(C = C) = 2E_{T}(C = C, 2sp^{3}) + E_{T}(C = C, \sigma)$$

$$= \begin{pmatrix} 2(-1.56513 \ eV) + \\ -\frac{2e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771)\left(2 - \frac{1}{2} \frac{a_{0}}{a}\right) \ln \frac{a + c'}{a - c'} - 1\right] + 16.20002 \ eV \end{pmatrix}$$

$$= 2(-1.56513 \ eV) + (-94.90610 \ eV)$$

$$= -98.03637 \ eV$$

$$(14.402)$$

#### VIBRATION OF ACETYLENE

15 The vibrational energy levels of CHCH may be solved as two equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

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# THE DOPPLER ENERGY TERMS OF THE C = C-BOND MO OF ACETYLENE

The equations of the radiation reaction force of the  $C \equiv C$ -bond MO are given by Eq. (14.231), except that the  $C \equiv C$ -bond MO parameters are used. The angular frequency of the 5 reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.5e^2}{4\pi\varepsilon_0 a^3}} = 2.00186 \, X \, 10^{16} \, rad/s \tag{14.403}$$

where a is given by Eq. (14.346). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.00186 \, X \, 10^{16} \, rad \, / \, s = 13.17659 \, eV$$
 (14.404)

10 In Eq. (11.181), substitution of  $E_T(C = C)/3$  (Eq. (14.402)) for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.404) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -32.67879 \ eV \sqrt{\frac{2e(13.17659 \ eV)}{m_e c^2}} = -0.23468 \ eV$$
 (14.405)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the  $C \equiv C$ -bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (14.405) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of the  $C \equiv C$  bond. Using the experimental  $C \equiv C = C = E_{vib}(v_3)$  of 3374 cm<sup>-1</sup> (0.41833 eV) [6] for  $\overline{E}_{Kvib}$  of the transition state having three bonds,  $\overline{E}'_{osc}(C \equiv C, \sigma)$  per bond is

$$\overline{E}'_{osc}(C \equiv C, \sigma) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(14.406)

$$\overline{E}'_{osc}(C \equiv C, \sigma) = -0.23468 \ eV + \frac{1}{2}(0.41833 \ eV) = -0.02551 \ eV$$
 (14.407)

Given that the vibration and reentrant oscillation is for three C-C bonds of the  $C \equiv C$  triple 25 bond,  $\overline{E}_{acetylene\ asc}(C \equiv C, \sigma)$ , is:

$$\overline{E}_{acetylene\ osc}\left(C \equiv C, \sigma\right) = 3\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$= 3\left(-0.23468\ eV + \frac{1}{2}(0.41833\ eV)\right)$$

$$= -0.07654\ eV$$
(14.408)

## TOTAL ENERGIES OF THE C = C-BOND MO OF ACETYLENE

 $E_{T+osc}(C \equiv C)$ , the total energy of the  $C \equiv C$ -bond MO including the Doppler term, is given 5 by the sum of  $E_T(C \equiv C)$  (Eq. (14.402)) and  $\overline{E}_{acetylene\ osc}(C \equiv C, \sigma)$  given by Eq. (14.408):

$$E_{T+osc}(C \equiv C) = \begin{pmatrix} V_e + T + V_m + V_p - E(C_{acetylene}, 2sp^3) \\ +2E_T(C \equiv C, 2sp^3) + \overline{E}_{acetylene \ asc}(C \equiv C, \sigma) \end{pmatrix}$$

$$= E_T(C \equiv C, \sigma) + 2E_T(C \equiv C, 2sp^3) + \overline{E}_{acetylene \ asc}(C \equiv C, \sigma)$$

$$= E_T(C \equiv C) + \overline{E}_{acetylene \ asc}(C \equiv C, \sigma)$$
(14.409)

$$E_{T+osc}\left(C \equiv C\right) = \begin{cases} \left(\frac{-3e^{2}}{8\pi\varepsilon_{0}c'} \left[\left(0.91771\right)\left(2 - \frac{1}{2}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right]\right) \\ -E\left(C_{acetylene}, 2sp^{3}\right) + 2E_{T}\left(C \equiv C, 2sp^{3}\right) \end{cases} \\ \left(1 + \left(3\right)\left(\frac{1}{3}\right)\sqrt{\frac{2\hbar\sqrt{\frac{1}{2}\frac{e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right) + 3\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{cases}$$

$$= -98.03637 \ eV - 3\left(0.23468 \ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$(14.410)$$

From Eqs. (14.408-14.410), the total energy of the  $C \equiv C$  -bond MO is

$$E_{T+osc}(C \equiv C) = -94.90610 \ eV + 2E_{T}(C \equiv C, 2sp^{3}) + \overline{E}_{acceptene \ asc}(C \equiv C, \sigma)$$

$$= -94.90610 \ eV + 2(-1.56513 \ eV) - 3\left(0.23468 \ eV - \frac{1}{2}(0.41833 \ eV)\right)$$

$$= -98.11291 \ eV$$
(14.411)

where the experimental  $E_{vib}$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

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#### BOND ENERGY OF THE C = C BOND OF ACETYLENE

As in the case of  $^{12}CH_2$  and  $^{14}NH$ , the dissociation of the  $C \equiv C$  bond forms three unpaired electrons per central atom wherein the magnetic moments cannot all cancel. The energy per atom E(magnetic) is given by Eq. (13.524). Thus, the dissociation energy of the  $C \equiv C$  bond of CHCH,  $E_D(HC \equiv CH)$ , is given by six times  $E(C,2sp^3)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each CH radical that forms the triple  $C \equiv C$  bond, minus the sum of  $\Delta E_{T+osc}(^{12}CH)$  (Eq. (14.396)), the energy change going from the hydrogen carbide radicals to the CH groups of acetylene,  $E_{T+osc}(C \equiv C)$  (Eq. (14.411)), and two times E(magnetic) given by Eq. (13.524). Thus, the dissociation energy of the  $C \equiv C$  bond of CHCH, is

$$\begin{split} E_D\left(HC \equiv CH\right) &= 6\left(E\left(C,2sp^3\right)\right) - \left(\Delta E_{T+osc}\left(^{12}CH\right) + E_{T+osc}\left(C \equiv C\right) + 2E(magnetic)\right) \\ &= 6\left(-14.63489\ eV\right) - \left(-0.06460\ eV - 98.11291\ eV + 0.29606\ eV\right) \\ &= 6\left(-14.63489\ eV\right) - \left(-97.88145\ eV\right) \\ &= 10.07212\ eV \end{split}$$

The experimental dissociation energy of the  $C \equiv C$  bond of CHCH is [7]

$$E_D(HC = CH) = 10.0014 \, eV$$
 (14.413)

The results of the determination of bond parameters of *CHCH* are given in Table 15 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

## BENZENE MOLECULE $(C_6H_6)$

20 The benzene molecule  $C_6H_6$  is formed by the reaction of three ethylene molecules:

$$3CH_2CH_2 \to C_6H_6 + 3H_2$$
 (14.414)

 $C_6H_6$  can be solved using the same principles as those used to solve ethylene wherein the 2s and 2p shells of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each  $2sp^3$  HO of each carbon atom initially has four unpaired electrons. Thus, the 6H atomic orbitals (AOs) of benzene contribute six electrons and the six  $sp^3$ -hybridized carbon

atoms contribute twenty-four electrons to form six C-H bonds and six C=C bonds. Each C-H bond has two paired electrons with one donated from the H AO and the other from the  $C2sp^3$  HO. Each C=C bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon atoms. Each C-H and each C=C bond comprises a linear combination of one and two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

#### FORCE BALANCE OF THE C = C-BOND MO OF BENZENE

 $C_6H_6$  can be considered a linear combination of three ethylene molecules wherein a 10 C-H bond of each  $CH_2$  group of  $H_2C=CH_2$  is replaced by a C=C bond to form a sixmember ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule  $(CH_2CH_2)$  section. Before forming ethylene groups, the  $2sp^3$  hybridized orbital arrangement of each carbon atom is given by Eq. (14.140). The sum  $E_T(C,2sp^3)$  of 15 calculated energies of C,  $C^{+}$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.141). The radius  $r_{2,m}$ , of the  $C2sp^3$  shell is given by Eq. (14.142). The Coulombic energy  $E_{Coulomb}(C, 2sp^3)$  and the energy  $E(C, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell are given by Eqs. (14.143) and (14.146), respectively. Two CH<sub>2</sub> radicals bond to form CH<sub>2</sub>CH<sub>2</sub> by forming a MO between the two pairs of remaining  $C2sp^3$ -HO electrons of the two carbon atoms. However, in this 20 case, the sharing of electrons between four C2sp3 HOs to form a MO comprising four spinpaired electrons permits each  $C2sp^3$  HO to decrease in radius and energy. The C=C-bond MO is a prolate-spheroidal-MO surface that cannot extend into C2sp3 HO for distances shorter than the radius of the C2sp3 shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the  $C2sp^3$  shell 25 at each C atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of each  $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as those of OH, NH, CH, the C=O-bond MO of  $CO_2$ , and the C-C-bond MO of  $CH_3CH_3$ , the C=Cbond MO of ethylene must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the C = C -bond MO must comprise

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a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$2(2C2sp^3 + 0.75 H_2 MO) \rightarrow C = C - bond MO$$
 (14.415)

5

The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution from each  $C2sp^3$  HO to the C=C-bond MO to achieve an energy minimum. The force balance of the C=C-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.415) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

The sharing of electrons between two pairs of  $C2sp^3$  HOs to form a C=C-bond MO permits each participating hybridized orbital to decrease in radius and energy. The sum  $E_T\left(C_{ethylene},2sp^3\right)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. 15 (14.243). In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating  $C2sp^3$  HO donates an excess of 25% of its electron density to the C=C-bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{ethylene2sp^3}$  of the  $C2sp^3$  shell of ethylene calculated 20 from the Coulombic energy is given by Eq. (14.244). The Coulombic energy  $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$  of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.245). The energy  $E\left(C_{ethylene},2sp^3\right)$  of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.246).  $E_T\left(C=C,2sp^3\right)$  (Eq. (14.247), the energy change of each  $C2sp^3$  shell with the formation of the C=C-bond MO is given by the difference between  $E\left(C_{ethylene},2sp^3\right)$  and  $E\left(C,2sp^3\right)$ .

Consider the case where three sets of C = C-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two  $C2sp^3$ HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$\begin{pmatrix}
3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C = C) - \text{ethylene-type-bond MO} \\
\rightarrow 6(C = C) - \text{bond MO of benzene}
\end{pmatrix} (14.416)$$

The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further 5 comprises an excess 25% charge-density contribution per bond from each  $C2sp^3$  HO to the C=C-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond C=C-bond are determined using the same equations as those used to determine the same parameters of the C=C-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene. The energies of each C=C bond of 10 benzene are also determined using the same equations as those of ethylene with the parameters of benzene. The result is that the energies are essentially given as 0.75 times the energies of the C=C-bond MO of ethylene (Eqs. (14.251-14.253) and (14.319-14.333).

The derivation of the dimensional parameters of benzene follows the same procedure as the determination of those of ethylene. As in the case of ethylene, each  $H_2$ -type ellipsoidal MO comprises 75% of the C=C-bond MO shared between two  $C2sp^3$  HOs corresponding to the electron charge density in Eq. (11.65) of  $\frac{-0.75e}{2}$ . But, the additional 25% charge-density contribution to each bond of the C=C-bond MO causes the electron charge density in Eq. (11.65) to be is given by  $\frac{-e}{2}=-0.5e$ . The corresponding force constant k' is given by Eq. (14.152). In addition, the energy matching at all six  $C2sp^3$  HOs further requires that k' be corrected by a hybridization factor (Eq. (13.430)) as in the case of ethylene, expect that the constraint that the bonds connect a six-member ring of C=C bonds of benzene rather two  $C2sp^3$  HOs of ethylene decreases the hybridization factor of benzene compared to that of ethylene (Eq. (14.248)).

Since the energy of each  $H_2$ -type ellipsoidal MO is matched to that of all the 25 continuously connected  $C_{benzene} 2sp^3$  HOs, the hybridization-energy-matching factor is 0.85252. Hybridization with 25% electron donation to each C = C-bond gives rise to the  $C_{benzene} 2sp^3$  HO-shell Coulombic energy  $E_{Coulomb} \left( C_{benzene}, 2sp^3 \right)$  given by Eq. (14.245). The corresponding hybridization factor is given by the ratio of 15.95955 eV, the magnitude of

 $E_{Coulomb}\left(C_{benzene},2sp^3\right)$  given by Eq. (14.245), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The hybridization energy factor  $C_{benzeneC2sp^3HO}$  is

$$C_{benzeneC2sp^3HO} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{benzene2sp^3}}} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.85252a_0}} = \frac{13.605804 \ eV}{15.95955 \ eV} = 0.85252 \quad (14.417)$$

Thus, the force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci (Eq. (11.65)) is given by

$$k' = C_{benzeneC2:\psi^3HO} \frac{(0.5)2e^2}{4\pi\varepsilon_0} = 0.85252 \frac{(0.5)2e^2}{4\pi\varepsilon_0}$$
 (14.418)

The distance from the origin to each focus c' is given by substitution of Eq. (14.418) into Eq. (13.60). Thus, the distance from the origin of the component of the double C = C -bond MO to each focus c' is given by

$$c' = a \sqrt{\frac{\hbar^2 4\pi \varepsilon_0}{(0.85252)m_e e^2 a}} = \sqrt{\frac{aa_0}{0.85252}}$$
 (14.419)

The internuclear distance from Eq. (14.419) is

$$2c' = 2\sqrt{\frac{aa_0}{0.85252}} \tag{14.420}$$

The length of the semiminor axis of the prolate spheroidal C = C-bond MO b = c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the C = C-bond MO. From the energy equation and the relationship between the axes, the dimensions of the C = C-bond MO are solved.

The general equations for the energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of the 20 C=C-bond MO of benzene are the same as those of the  $CH_2CH_2$  MO except that energy of the  $C_{benzene}2sp^3$  HO is used and the hybridization factor is given by Eq. (14.417). Using Eqs. (14.251) and (14.417),  $E_T(C=C,\sigma)$  is given by

$$E_{T}(C=C,\sigma) = E_{T} + E(C_{benzene}, 2sp^{3}) - E(C_{benzene}, 2sp^{3})$$

$$= -\frac{2e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.85252) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right]$$
(14.421)

The total energy term of the double C=C-bond MO is given by the sum of the two  $H_2$ -type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition,  $E_T(C=C,\sigma)$  given by Eq. (14.421) is set equal to two times Eq. (13.75):

$$E_T(C=C,\sigma) = -\frac{2e^2}{8\pi\epsilon_0 c'} \left[ (0.85252) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] = -63.27074 \ eV$$
 (14.422)

5 From the energy relationship given by Eq. (14.422) and the relationship between the axes given by Eqs. (14.419-14.420) and (13.62-13.63), the dimensions of the C = C-bond MO can be solved.

Substitution of Eq. (14.419) into Eq. (14.422) gives

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{0.85252}}}\left[(0.85252)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{0.85252}}}{a-\sqrt{\frac{aa_0}{0.85252}}}-1\right] = e63.27074 \qquad (14.423)$$

10 The most convenient way to solve Eq. (14.423) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.47348a_0 = 7.79733 \times 10^{-11} m \tag{14.424}$$

Substitution of Eq. (14.424) into Eq. (14.4129) gives

$$c' = 1.31468a_0 = 6.95699 \ X \ 10^{-11} \ m \tag{14.425}$$

15 The internuclear distance given by multiplying Eq. (14.425) by two is

$$2c' = 2.62936a_0 = 1.39140 \ X \ 10^{-10} \ m \tag{14.426}$$

The experimental bond distance is [3]

$$2c' = 1.339 X 10^{-10} m ag{14.427}$$

Substitution of Eqs. (14.424-14.425) into Eq. (13.62) gives

$$b = c = 0.66540a_0 = 3.52116 \times 10^{-11} m \tag{14.428}$$

Substitution of Eqs. (14.424-14.425) into Eq. (13.63) gives

$$e = 0.89223 \tag{14.429}$$

The nucleus of the C atoms comprise the foci of the  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{benzene} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). Each benzene carbon atom contributes  $(0.75)(-1.13380 \ eV) = -0.85035 \ eV$  (Eqs. (14.483) and (14.493)) to each of the two C = C-bond MOs and  $(0.5)(-1.13380 \ eV) = -0.56690 \ eV$  (Eq. (14.467)) to the corresponding

C-H-bond MO. The energy contribution due to the charge donation at each carbon superimposes linearly. The radius of  $r_{benzene2sp^3} = 0.79597a_0$  is calculated using Eq. (14.518) using the total energy donation to each bond with which it is participates in bonding. The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{benzene2sp^3} = 0.79597a_0$  is the

5 radius of the  $C_{benzene} 2sp^3$  shell. Substitution of Eqs. (14.424-14.425) into Eq. (13.261) gives  $\theta' = 134.24^{\circ}$  (14.430)

Then, the angle  $\theta_{C=C_{bracene}2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C=C_{berren}, 2sp^3HO} = 180^{\circ} - 134.24^{\circ} = 45.76^{\circ}$$
 (14.431)

10 as shown in Figure 45.

Thus, the  $^{12}CH_4$  bond dissociation energy,  $E_D(^{12}CH_4)$ , given by Eqs. (13.154), and (13.614-13.616) is

$$E_{D}(^{12}CH_{4}) = -(67.95529 \ eV + 13.59844 \ eV) - E_{T+asc}(^{12}CH_{4})$$

$$= -81.55373 \ eV - (-86.04373 \ eV)$$

$$= 4.4900 \ eV$$
(13.617)

The experimental  $^{12}CH_4$  bond dissociation energy is [40]

15 
$$E_D(^{12}CH_4) = 4.48464 \, eV$$
 (13.618)

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C=C_{beauter},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with each  $C_{beauter} 2sp^3$  radial vector obeys the following relationship:

 $r_{bernene 2.sp^3} \sin \theta_{C = C_{bernene} 2.sp^3 HO} = 0.79597 a_0 \sin \theta_{C = C_{bernene} 2.sp^3 HO} = b \sin \theta_{C = C_{bernene} .H_2 MO}$ (14.432) such that

$$\theta_{C=C_{bencens},H_2MO} = \sin^{-1} \frac{0.79597a_0 \sin \theta_{C=C_{bencens} 2sp^3HO}}{b} = \sin^{-1} \frac{0.79597a_0 \sin 45.76^{\circ}}{b} \quad (14.433)$$

with the use of Eq. (14.431). Substitution of Eq. (14.428) into Eq. (14.433) gives

$$\theta_{C=C_{brown}, H_2MO} = 58.98^{\circ} \tag{14.434}$$

25 Then, the distance  $d_{C=C_{beauto},H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C=C_{L_{1},M,MO}} = a\cos\theta_{C=C_{L_{1},M,MO}} \tag{14.435}$$

Substitution of Eqs. (14.424) and (14.434) into Eq. (14.435) gives

$$d_{C=C_{location}, H_2MO} = 0.75935 a_0 = 4.01829 X 10^{-11} m$$
 (14.436)

The distance  $d_{C=C_{lemens}2:p^3HO}$  along the internuclear axis from the origin of the C atom to the 5 point of intersection of the orbitals is given by

$$d_{C=C_{1},...,2sp^{3}HO} = c' - d_{C=C_{bemoss},H_{2}MO}$$
(14.437)

Substitution of Eqs. (14.425) and (14.436) into Eq. (14.437) gives

$$d_{C=C_{brurne} 2sp^3HO} = 0.55533a_0 = 2.93870 X 10^{-11} m$$
 (14.438)

#### 10 FORCE BALANCE OF THE CH MOS OF BENZENE

Benzene can also be considered as comprising chemical bonds between six *CH* radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of *CH* is given in the Hydrogen Carbide (*CH*) section. Each *C-H* bond of *CH* having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO as given by Eq. (13.439):

$$1 C2sp^3 + 0.75 H_2 MO \rightarrow CH MO$$
 (14.439)

20 The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of  $H_2$ , the C-H-bond MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the  $C2sp^3$  shell at the C atom whose nucleus serves as the other focus.

The force balance of the CH MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.439) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO. The force constant k' to determine the ellipsoidal parameter c' of the each  $H_2$ -type-ellipsoidal-MO component 30 of the CH MO in terms of the central force of the foci is given by Eq. (13.59). The distance

from the origin of each C-H-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each C-H-bond MO. From the energy equation and the relationship between the axes, the dimensions of the CH MO are solved.

Consider the formation of the double C = C-bond MOs of benzene wherein ethylene formed from two  $CH_2$  radicals, each having a  $C2sp^3$  shell with an energy given by Eq. (14.146), serves as a basis element. The energy components of  $V_s$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  are 10 the same as those of the hydrogen carbide radical, except that  $E_T(C = C, 2sp^3)$  is subtracted from  $E_T(CH)$  of Eq. (13.495). As in the case of the  $CH_2$  groups of ethylene (Eq. (14.270)), the subtraction of the energy change of the  $C2sp^3$  shell per H with the formation of the C=C-bond MO matches the energy of each C-H-bond MO to the decrease in the energy of the corresponding  $C2sp^3$  HO. Using Eqs. (13.431) and (14.247),  $E_{T_{beaumag}}(CH)$  is given by

$$E_{T_{\text{becomes}}}(CH) = E_T + E(C, 2sp^3) - E_T(C = C, 2sp^3)$$

$$= \left( -\frac{e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \right)$$

$$-14.63489 \ eV - \left( -1.13379 \ eV \right)$$
(14.440)

 $E_{T_{beautor}}$  (CH) given by Eq. (14.440) is set equal to the energy of the  $H_2$ -type ellipsoidal MO given by Eq. (13.75):

$$E_{T_{beausse}}(CH) = \begin{pmatrix} -\frac{e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \\ -14.63489 \ eV - (-1.13379 \ eV) \end{pmatrix} = -31.63537 \ eV$$
(14.441)

20 From the energy relationship given by Eq. (14.441) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.441) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e18.13427$$
(14.442)

15

The most convenient way to solve Eq. (14.442) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.60061a_0 = 8.47006 \ X \ 10^{-11} \ m \tag{14.443}$$

Substitution of Eq. (14.443) into Eq. (14.60) gives

5 
$$c' = 1.03299a_0 = 5.46636 \times 10^{-11} m$$
 (14.444)

The internuclear distance given by multiplying Eq. (14.444) by two is

$$2c' = 2.06598a_0 = 1.09327 \times 10^{-10} m \tag{14.445}$$

The experimental bond distance is [3]

$$2c' = 1.101 \ X \ 10^{-10} \ m \tag{14.446}$$

10 Substitution of Eqs. (14.443-14.444) into Eq. (14.62) gives

$$b = c = 1.22265a_0 = 6.47000 X 10^{-11} m ag{14.447}$$

Substitution of Eqs. (14.443-14.444) into Eq. (14.63) gives

$$e = 0.64537 \tag{14.448}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each 15  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{benzene} 2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta$ ' is given by Eq. (13.261) where  $r_n = r_{benzene2sp^3} = 0.79597a_0$  is the radius of the  $C_{benzene} 2sp^3$  shell. Substitution of Eqs. (14.443-14.444) into Eq. (13.261) gives

$$\theta' = 74.42^{\circ} \tag{14.449}$$

Then, the angle  $\theta_{C-H_{\text{bearen}}2:p^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

$$\theta_{C-H_{becom}} = 180^{\circ} - 74.42^{\circ} = 105.58^{\circ}$$
 (14.450)

as shown in Figure 46.

25

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{basins},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{besterns} 2sp^3$  radial vector obeys the following relationship:

$$r_{benzene2sp^3} \sin \theta_{C-H_{benzene}2sp^3HO} = 0.79597 a_0 \sin \theta_{C-H_{benzene}2sp^3HO} = b \sin \theta_{C-H_{benzene},H_{2}MO}$$
 (14.451)

such that

$$\theta_{C-H_{benzene},H_2MO} = \sin^{-1} \frac{0.79597a_0 \sin \theta_{C-H_{benzene} 2sp^3HO}}{b} = \sin^{-1} \frac{0.79597a_0 \sin 105.58^{\circ}}{b} (14.452)$$

with the use of Eq. (14.450). Substitution of Eq. (14.447) into Eq. (14.452) gives

$$\theta_{C-H_{benzes}, H_2MO} = 38.84^{\circ} \tag{14.453}$$

5 Then, the distance  $d_{C-H_{bosons},H_1MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{berzers},H_2MO} = a\cos\theta_{C-H_{berzers},H_2MO} \tag{14.454}$$

Substitution of Eqs. (14.443) and (14.453) into Eq. (14.454) gives

$$d_{C-H_{bosone},H_2MO} = 1.24678a_0 = 6.59767 X 10^{-11} m$$
 (14.455)

10 The distance  $d_{C-H_{lement}2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{boxes} 2sp^{2}HO} = d_{C-H_{boxes}, H_{2}MO} - c'$$
(14.456)

Substitution of Eqs. (14.444) and (14.455) into Eq. (14.456) gives

$$d_{C-H_{beauss} 2:p^3HO} = 0.21379a_0 = 1.13131 \ X \ 10^{-11} \ m \tag{14.457}$$

15 The basis set of benzene, the ethylene molecule, is planar with bond angles of approximately  $120^{\circ}$  (Eqs. (14.298-14.302)). To form a closed ring of equivalent planar bonds, the C=C bonds of benzene form a planar hexagon. The bond angle  $\theta_{C=C=C}$  between the internuclear axis of any two adjacent C=C bonds is

$$\theta_{C=C=C} = 120^{\circ}$$
 (14.458)

20 The bond angle  $\theta_{C=C-H}$  between the internuclear axis of each C=C bond and the corresponding H atom of each CH group is

$$\theta_{C=C-H} = 120^{\circ} \tag{14.459}$$

The experimental angle between the C = C = C bonds is [13-15]

$$\theta_{C=C=C} = 120^{\circ}$$
 (14.460)

25 The experimental angle between the C = C - H bonds is [13-15]

$$\theta_{C=C-H} = 120^{\circ}$$
 (14.461)

The  $C_6H_6$  MO shown in Figure 47 was rendered using these parameters.

The charge-density in the C=C-bond MO is increased by a factor of 0.25 per bond with the formation of the  $C_{benzene} 2sp^3$  HOs each having a smaller radius. Using the orbital

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composition of the CH groups (Eq. (14.439)) and the C = C-bond MO (Eq. (14.416), the radii of  $Cls = 0.17113a_0$  (Eq. (10.51)) and  $C_{bemzene}2sp^3 = 0.79597a_0$  (Eq. (14.520)) shells, and the parameters of the C = C-bond (Eqs. (13.3-13.4), (14.424-14.426), and (14.428-14.438)), the parameters of the C - H-bond MOs (Eqs. (13.3-13.4), (14.443-14.445), and 5 (14.447-14.457)), and the bond-angle parameters (Eqs. (14.458-14.459)), the charge-density of the  $C_6H_6$  MO comprising the linear combination of six sets of C - H-bond MOs with bridging C = C-bond MOs is shown in Figure 47. Each C - H-bond MO comprises a  $H_2$ -type ellipsoidal MO and a  $C_{benzene}2sp^3$  HO having the dimensional diagram shown in Figure 46. The C = C-bond MO comprises a  $H_2$ -type ellipsoidal MO bridging two sets of two  $C_{benzene}2sp^3$  HOs having the dimensional diagram shown in Figure 45.

#### ENERGIES OF THE CH GROUPS

The energies of each CH group of benzene are given by the substitution of the semiprincipal axes (Eqs. (14.443-14.444) and (14.447)) into the energy equations of hydrogen carbide (Eqs. (13.449-13.453)), with the exception that  $E_T(C = C, 2sp^3)$  (Eq. (14.247)) is subtracted from  $E_T(CH)$  in Eq. (13.453):

$$V_{e} = (0.91771) \frac{-2e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} = -37.10024 \, eV$$
 (14.462)

$$V_p = \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 13.17125 \, eV \tag{14.463}$$

$$T = (0.91771) \frac{\hbar^2}{2m \cdot a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 11.58941 \ eV$$
 (14.464)

20 
$$V_{m} = (0.91771) \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -5.79470 \ eV$$
 (14.465)

$$E_{T_{benzens}}(CH) = \begin{pmatrix} -\frac{e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \\ -14.63489 \ eV - \left( -1.13379 \ eV \right) \end{pmatrix} = -31.63539 \ eV$$

(14.466)

where  $E_{T_{berrent}}$  (CH) is given by Eq. (14.440) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

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The total energy of the C-H-bond MO,  $E_{T_{beams}}(C-H)$ , is given by the sum of  $0.5E_T(C=C,2sp^3)$ , the energy change of each  $C2sp^3$  shell per single bond due to the decrease in radius with the formation of the corresponding C=C-bond MO (Eq. (14.247)), and  $E_{T_{beams}}(CH)$ , the  $\sigma$  MO contribution given by Eq. (14.441):

$$E_{T_{beaucros}}(C-H) = (0.5)E_{T}(C=C,2sp^{3}) + E_{T_{beaucros}}(CH)$$

$$= \begin{pmatrix} (0.5)(-1.13379 \ eV) + \\ -\frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771)\left(2 - \frac{1}{2}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] \\ -14.63489 \ eV - (-1.13379 \ eV) \end{pmatrix}$$

$$= (0.5)(-1.13379 \ eV) + (-31.63537 \ eV)$$

$$= -32.20226 \ eV$$

$$(14.467)$$

#### VIBRATION OF THE 12CH GROUPS

The vibrational energy levels of *CH* in benzene may be solved using the methods given in the Vibration and Rotation of *CH* section.

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## THE DOPPLER ENERGY TERMS OF THE 12CH GROUPS

The equations of the radiation reaction force of the CH groups in benzene are the same as those of the hydrogen carbide radical with the substitution of the CH-group parameters. Using Eq. (13.477), the angular frequency of the reentrant oscillation in the transition state is

15 
$$\omega = \sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}} = 2.64826 \, X \, 10^{16} \, rad/s \tag{14.468}$$

where b is given by Eq. (14.447). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar \omega = \hbar 2.64826 \, X \, 10^{16} \, rad \, / \, s = 17.43132 \, eV$$
 (14.469)

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total 20 energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.469) for  $\overline{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(17.43132 \ eV)}{m_e c^2}} = -0.26130 \ eV$$
 (14.470)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (14.470) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of the C-H bond. Using  $\omega_e$  given by Eq. (13.458) for  $\overline{E}_{Kvib}$  of the transition,  $\overline{E}_{benzene\ osc}$  (12CH) per bond is

$$\overline{E}_{benzens \ osc} \left(^{12}CH\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}$$
(14.471)

10 
$$\overline{E}_{benzene \ osc} \left( ^{12}CH \right) = -0.26130 \ eV + \frac{1}{2} \left( 0.35532 \ eV \right) = -0.08364 \ eV$$
 (14.472)

## TOTAL AND BOND ENERGIES OF THE 12CH GROUPS

 $E_{benzeneT+osc}$  (12CH), the total energy of each 12CH group including the Doppler term, is given by the sum of  $E_{T_{benzene}}$  (C-H) (Eq. (14.467)) and  $\bar{E}_{benzene\ osc}$  (12CH) given by Eq. (14.472):

$$E_{benzeneT+osc}\left(CH\right) = \begin{pmatrix} \left(V_e + T + V_m + V_p + E\left(C, 2sp^3\right) - E_T\left(C = C, 2sp^3\right)\right) \\ +0.5E_T\left(C = C, 2sp^3\right) + \overline{E}_{benzene\ osc}\left(^{12}CH\right) \end{pmatrix}$$

$$= E_{T_{benzene}}\left(C - H\right) + \overline{E}_{benzene\ osc}\left(^{12}CH\right)$$
(14.473)

$$E_{benzeneT+asc} \binom{12CH}{=} \begin{cases} \left(\frac{-e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left(2 - \frac{1}{2} \frac{a_0}{a}\right) \ln \frac{a + c'}{a - c'} - 1\right] \right) - 0.5(1.13379 \, eV) \\ \left(-14.63489 \, eV - (-1.13379 \, eV) \right) \\ \left(\frac{2\hbar \sqrt{\frac{3}{4} \frac{e^2}{4\pi\varepsilon_0 b^3}}}{m_e} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}\right) \end{cases}$$

$$= -32.20226 \, eV - \left(0.26130 \, eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}\right)$$

$$(14.474)$$

From Eqs. (14.472-14.474), the total energy of each  $^{12}CH$  is

$$E_{benzeneT+osc} {}^{398}$$

$$E_{benzeneT+osc} {}^{(12}CH) = -32.20226 \ eV + \overline{E}_{benzene \ osc} {}^{(12}CH_2)$$

$$= -32.20226 \ eV - \left(0.26130 \ eV - \frac{1}{2}(0.35532 \ eV)\right)$$

$$= -32.28590 \ eV$$
(14.475)

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

As in the case of  $^{12}CH_2$ ,  $^{14}NH$ , and acetylene, the dissociation of the C=C bonds forms three unpaired electrons per central atom wherein the magnetic moments cannot all 5 cancel. The energy per atom E(magnetic) is given by Eq. (13.524). Thus, the bond dissociation energy of each CH group of the linear combination to form benzene,  $E_{D_{benzene}} \left( ^{12}CH \right)$ , is given by the sum of the total energies of the  $C2sp^3$  HO and the hydrogen atom minus the sum of  $E_{benzeneT+osc} \left( ^{12}CH \right)$  and E(magnetic) given by Eq. (13.524):

$$E_{D_{benzens}} \left( ^{12}CH \right) = E\left( C, 2sp^{3} \right) + E(H) - \left( E_{benzensT+osc} \left( ^{12}CH \right) + E(magnetic) \right)$$
 (14.476)

10  $E(C, 2sp^3)$  is given by Eq. (13.428),  $E_D(H)$  is given by Eq. (13.154), and E(magnetic) is given by Eq. (13.524). Thus,  $E_{D_{beautre}}$  (12CH) given by Eqs. (13.154), (13.428), (13.524), (14.475), and (14.476) is

$$E_{D_{benzens}} {12CH} = -(14.63489 \ eV + 13.59844 \ eV) - (E_{benzeneT+osc} (CH) + E(magnetic))$$

$$= -28.23333 \ eV - (-32.28590 \ eV + 0.14803 \ eV)$$

$$= 3.90454 \ eV$$
(14.477)

## 15 SUM OF THE ENERGIES OF THE C=C $\sigma$ MO ELEMENT AND THE HOS OF BENZENE

The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of the C=C-bond MO of benzene are the same as those of the  $CH_2CH_2$  MO except that the hybridization factor is given by Eq. (14.417). The energies of each C=C-bond MO are given by the substitution of the 20 semiprincipal axes (Eqs. (14.424-14.425) and (14.428)) into energy equations of the  $CH_2CH_2$  MO (Eqs. (14.319-14.323)), with the exception that the hybridization factor is 0.85252 (Eq. (14.417)):

$$V_e = 2(0.85252) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -101.12679 \ eV$$
 (14.478)

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$$V_p = 2 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 20.69825 \ eV \tag{14.479}$$

$$T = 2(0.85252) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 34.31559 \ eV$$
 (14.480)

$$V_m = 2(0.85252) \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -17.15779 \ eV$$
 (14.481)

$$E_T(C=C,\sigma) = -\frac{2e^2}{8\pi\varepsilon_0 c'} \left[ (0.85252) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] = -63.27075 \ eV \ (14.482)$$

5 where  $E_T(C=C,\sigma)$  is the total energy of the C=C  $\sigma$  MO given by Eq. (14.421) which is reiteratively matched to two times Eq. (13.75) within five-significant-figure round off error.

The total energy of the C=C-bond MO,  $E_T(C=C)$ , is given by the sum of two times  $E_T(C=C,2sp^3)$ , the energy change of each  $C2sp^3$  shell due to the decrease in radius with the formation of the C=C-bond MO (Eq. (14.247)), and  $E_T(C=C,\sigma)$ , the  $\sigma$  MO contribution given by Eq. (14.422):

$$E_{T}(C=C) = 2E_{T}(C=C,2sp^{3}) + E_{T}(C=C,\sigma)$$

$$= \begin{pmatrix} 2(-1.13380 \ eV) + \\ \left( -\frac{2e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.85252) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] \right)$$

$$= 2(-1.13380 \ eV) + (-63.27074 \ eV) = -65.53833 \ eV$$

$$(14.483)$$

which is the same  $E_T(C=C,\sigma)$  of ethylene given by Eq. (14.324).

#### VIBRATION OF BENZENE

15 The C = C vibrational energy levels of  $C_6H_6$  may be solved as six sets of equivalent coupled harmonic oscillators where each C is a further coupled to the corresponding C - H oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of 20 Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE C = C-BOND MO ELEMENT

### OF BENZENE

The equations of the radiation reaction force of the C = C-bond MO of benzene are given by Eq. (13.142), except the force-constant factor is (0.85252)0.5 based on the force constant k' of Eq. (14.418), and the C = C-bond MO parameters are used. The angular frequency of the 5 reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.85252 \frac{(0.5)e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 4.97272 \times 10^{16} \text{ rad/s}$$
 (14.484)

where b is given by Eq. (14.428). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 4.97272 \, X \, 10^{16} \, rad \, / \, s = 32.73133 \, eV$$
 (14.485)

10 In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.485) for  $\overline{E}_K$  gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63536831 \ eV \sqrt{\frac{2e(32.73133 \ eV)}{m_e c^2}} = -0.35806 \ eV \tag{14.486}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the C = C-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (14.486) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of the C = C bond. Using the experimental C = C  $E_{vib}(v_{16})$  of 1584.8  $cm^{-1}$  (0.19649 eV) [16] for  $\overline{E}_{Kvib}$  of the transition state having two bonds,  $\overline{E}_{osc}^{+}$  (C = C,  $\sigma$ ) per bond is

$$\overline{E}'_{osc}(C=C,\sigma) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(14.487)

$$\overline{E}'_{osc}(C=C,\sigma) = -0.35806 \ eV + \frac{1}{2}(0.19649 \ eV) = -0.25982 \ eV$$
 (14.488)

Given that the vibration and reentrant oscillation is for two C-C bonds of each C=C double bond,  $\overline{E}_{benzens \ osc}(C=C,\sigma)$ , is:

$$\overline{E}_{benzene \ osc} \left( C = C, \sigma \right) = 2 \left( \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) = 2 \left( -0.35806 \ eV + \frac{1}{2} \left( 0.19649 \ eV \right) \right) = -0.51963 \ eV$$
(14.489)

5

#### TOTAL ENERGIES OF THE C = C-BOND MO ELEMENT OF BENZENE

 $E_{T+asc}(C=C)$ , the total energy of the C=C-bond MO of benzene including the Doppler term, is given by the sum of  $E_T(C=C)$  (Eq. (14.483)) and  $\overline{E}_{benzene\ osc}(C=C,\sigma)$  given by Eq. (14.489):

$$E_{T+osc}(C=C) = V_e + T + V_m + V_p + 2E_T(C=C, 2sp^3) + \overline{E}_{benzene \ osc}(C=C, \sigma)$$

$$= E_T(C=C, \sigma) + 2E_T(C=C, 2sp^3) + \overline{E}_{benzene \ osc}(C=C, \sigma)$$

$$= E_T(C=C) + \overline{E}_{benzene \ osc}(C=C, \sigma)$$
(14.490)

$$E_{T+osc}(C=C) = \begin{cases} \left(\frac{-2e^2}{8\pi\varepsilon_0 c'}\right) \left[ (0.85252) \left(2 - \frac{1}{2} \frac{a_0}{a}\right) \ln \frac{a+c'}{a-c'} - 1\right] + 2E_T\left(C=C, 2sp^3\right) \\ \left(\frac{2\hbar\sqrt{\frac{(0.85252)\frac{1}{2} \frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}}{\frac{m_e}{m_e c^2}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \end{cases}$$

$$= -65.53833 \ eV - 2\left(0.35806 \ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$(14.491)$$

From Eqs. (14.489-14.491), the total energy of the C = C -bond MO is

$$\begin{split} E_{T+osc}\left(C=C\right) &= -63.27074 \ eV + 2E_{T}\left(C=C,2sp^{3}\right) + \overline{E}_{benzene\ osc}\left(C=C,\sigma\right) \\ &= -63.27074 \ eV + 2\left(-1.13380\ eV\right) - 2\left(0.35806\ eV - \frac{1}{2}\left(0.19649\ eV\right)\right) \\ &= -66.05796\ eV \end{split} \tag{14.492}$$

15

where the experimental  $E_{vib}$  was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

## TOTAL BOND DISSOCIATION ENERGY OF BENZENE

Ethylene serves as a basis element for the C=C bonding of benzene wherein each of the six C=C bonds of benzene comprises (0.75)(4)=3 electrons according to Eq. (14.416). The total energy of the bonds of the eighteen electrons of the C=C bonds of benzene,  $E_T\left(C_6H_6,C=C\right)$ , is given by (6)(0.75) times  $E_{T+ase}\left(C=C\right)$  (Eq. (14.492)), the total energy of the C=C-bond MO of benzene including the Doppler term, minus eighteen times  $E\left(C,2sp^3\right)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each C that forms the double C=C bonds. Thus, the total energy of the six C=C bonds of benzene is

$$E_{T}\left(C_{6}H_{6}, C = C\right) = (6)(0.75)E_{T+osc}\left(C = C\right) - 18E\left(C, 2sp^{3}\right)$$

$$= (6)(0.75)(-66.05796 \ eV) - 18(-14.63489 \ eV)$$

$$= -297.26081 \ eV - \left(-263.42798 \ eV\right)$$

$$= -33.83284 \ eV$$
(14.493)

10 Each of the C-H bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each C-H bond,  $-E_{D_{benzene}}$  (12CH) (Eq. (14.477)), the total energy of the twelve electrons of the six C-H bonds of benzene,  $E_T(C_6H_6, C-H)$ , is given by

$$E_T(C_6H_6,C-H) = (6)(-E_{D_{beautre}}(^{12}CH)) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV} (14.494)$$

The total bond dissociation energy of benzene,  $E_D(C_6H_6)$ , is given by the negative sum of

15 
$$E_T\left(C_6H_6, C=C\right)$$
 (Eq. (14.493)) and  $E_T\left(C_6H_6, C-H\right)$  (Eq. (14.494)):

$$E_D(C_6H_6) = -\left(E_T\left(C_6H_6, C = C\right) + E_T\left(C_6H_6, C - H\right)\right)$$

$$= -\left(\left(-33.83284 \ eV\right) + \left(-23.42724 \ eV\right)\right)$$

$$= 57.2601 \ eV$$
(14.495)

The experimental total bond dissociation energy of benzene,  $E_T(C_6H_6)$ , is given by the negative difference between the enthalpy of its formation  $(\Delta H_f(benzene(gas)))$  and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen 20  $(\Delta H_f(H(gas)))$  atoms. The heats of formation are [17-18]

$$\Delta H_f \left( benzene \left( gas \right) \right) = 82.9 \ kJ / mole \left( 0.8592 \ eV / molecule \right) \tag{14.496}$$

$$\Delta H_f(C(gas)) = 716.68 \, kJ \, / \, mole \, (7.42774 \, eV \, / \, molecule)$$
 (14.497)

$$\Delta H_f(H(gas)) = 217.998 \, kJ / mole (2.259353 \, eV / molecule)$$
 (14.498)

Thus, the total bond dissociation energy of benzene,  $E_D(C_6H_6)$ , is

$$E_{D}(C_{6}H_{6}) - E_{T}(C_{6}H_{6}) = -(\Delta H_{f}(benzene(gas)) - (6\Delta H_{f}(C(gas)) + 6\Delta H_{f}(H(gas))))$$

$$= -(0.8592 \text{ eV} - 6(7.42774 \text{ eV} + 2.259353 \text{ eV}))$$

$$= 57.26 \text{ eV}$$

5 (14.499)

where  $E_T(C_6H_6)$  is the total energy of the bonds. The results of the determination of bond parameters of  $C_6H_6$  are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

10

### **CONTINUOUS-CHAIN ALKANES** $(C_n H_{2n+2}, n=3,4,5...\infty)$

The continuous chain alkanes,  $C_nH_{2n+2}$ , are the homologous series comprising terminal methyl groups at each end of the chain with n-2 methylene  $(CH_2)$  groups in between:

$$CH_3(CH_2)_{r=2}CH_3$$
 (14.500)

- 15  $C_nH_{2n+2}$  can be solved using the same principles as those used to solve ethane and ethylene wherein the 2s and 2p shells of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three H AOs combine with three carbon  $2sp^3$  HOs and two H AOs combine with two carbon  $2sp^3$  HOs to form each methyl and methylene group, respectively, where
- with two carbon  $2sp^3$  HOs to form each methyl and methylene group, respectively, where each bond comprises a  $H_2$ -type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The  $CH_3$  and  $CH_2$  groups bond by forming  $H_2$ -type MOs between the remaining  $C2sp^3$  HOs on the carbons such that each carbon forms four bonds involving its four  $C2sp^3$  HOs.

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# FORCE BALANCE OF THE C-C-BOND MOs OF CONTINUOUS-CHAIN ALKANES

 $C_n H_{2n+2}$  comprises a chemical bond between two terminal  $CH_3$  radicals and n-2  $CH_2$  radicals wherein each methyl and methylene radical comprises three and two chemical bonds, respectively, between carbon and hydrogen atoms. The solution of the parameters of  $CH_3$  is given in the Methyl Radical  $(CH_3)$  section. The solution of the parameters of  $CH_2$  is given in the Dihydrogen Carbide Radical  $(CH_2)$  section and follows the same procedure. Each C-H bond having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO as given by Eq. (13.429):

$$1 C2sp^3 + 0.75 H, MO \rightarrow C - H MO$$
 (14.501)

The proton of the H atom and the nucleus of the C atom are along each internuclear axis 15 and serve as the foci. As in the case of  $H_2$ , each of the C-H-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into C2sp3 HO for distances shorter than the radius of the C2sp3 shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the  $C2sp^3$  shell at the C atom whose nucleus serves as the other focus. The electron 20 configuration and the energy,  $E(C,2sp^3)$ , of the  $C2sp^3$  shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each C-H bond is provided by the spin-pairing force of the CH<sub>3</sub> or CH<sub>2</sub> MO that has the symmetry of an s orbital that superimposes with the C2sp3 orbitals such that the corresponding angular momenta are unchanged. The energies of each  $CH_3$  and  $CH_2$  MO involve each  $C2sp^3$  and 25 each H1s electron with the formation of each C-H bond. The sum of the energies of the  $H_2$ -type ellipsoidal MOs is matched to that of the  $C2sp^3$  shell. The force balance of the C-H-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.139) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

The  $CH_3$  and  $CH_2$  groups form C-C bonds comprising  $H_2$ -type MOs between the remaining  $C2sp^3$  HOs on the carbons such that each carbon forms four bonds involving its four  $C2sp^3$  HOs. The sharing of electrons between any two  $C2sp^3$  HOs to form a molecular orbital (MO) comprising two spin-paired electrons permits each  $C2sp^3$  HO to decrease in radius and energy. As in the case of the C-H bonds, each C-C-bond MO is a prolate-spheroidal-MO surface that cannot extend into  $C2sp^3$  HO for distances shorter than the radius of the  $C2sp^3$  shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the  $C2sp^3$  shell at each C atom. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $C2sp^3$  shell. As 10 in the case of previous examples of energy-matched MOs such as the C-C-bond MO of ethane, each C-C-bond MO of  $C_nH_{2m+2}$  must comprise 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the C-C-bond MO must comprise two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the two  $C2sp^3$  HOs:

15

$$2 C2sp^3 + 0.75 H_2 MO \rightarrow C - C - bond MO$$
 (14.502)

The linear combination of the  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution from each  $C2sp^3$  HO to the C-C-20 bond MO to achieve an energy minimum. The force balance of the C-C-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.502) and the energy matching condition between the  $C2sp^3$ -HO components of the MO.

Before bonding, the  $2sp^3$  hybridized orbital arrangement of each carbon atom is given by Eq. (14.140). The sum  $E_T(C,2sp^3)$  of calculated energies of C,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.141). The radius  $r_{2sp^3}$  of the  $C2sp^3$  shell is given by Eq. (14.142). The Coulombic energy  $E_{Coulomb}(C,2sp^3)$  and the energy  $E(C,2sp^3)$  of the outer electron of the  $C2sp^3$  shell are given by Eqs. (14.143) and (14.146), respectively.

The formation of each C-C bond of  $C_nH_{2n+2}$  further requires that the energy of all

H<sub>2</sub>-type prolate spheroidal MOs (σ MOs) be matched at all C2sp³ HOs since they are continuous throughout the molecule. Thus, the energy of each C2sp³ HO must be a linear combination of that of the CH<sub>3</sub> and CH<sub>2</sub> groups that serve as basis elements. Each CH<sub>3</sub> forms one C-C bond, and each CH<sub>2</sub> group forms two. Thus, the energy of each C2sp³ HO of each CH<sub>3</sub> and CH<sub>2</sub> group alone is given by that in ethane and ethylene, respectively. The parameters of ethane and ethylene are given by Eqs. (14.147-14.151) and (14.244-14.247), respectively. The alkane parameters can be determined by first reviewing those of ethane and ethylene.

With the formation of the C-C-bond MO of ethane from two methyl radicals, each 10 having a  $C2sp^3$  electron with an energy given by Eq. (14.146), the total energy of the state is given by the sum over the four electrons. The sum  $E_T\left(C_{ethans}, 2sp^3\right)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  given by Eq. (14.147), is

$$\begin{split} E_T\left(C_{ethane}, 2sp^3\right) &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + E\left(C, 2sp^3\right)\right) \\ &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + 14.63489\ eV\right)(14.503) \\ &= -151.61569\ eV \end{split}$$

where  $E(C,2sp^3)$  is the sum of the energy of C,  $-11.27671\,eV$ , and the hybridization 15 energy. The orbital-angular-momentum interactions also cancel such that the energy of the  $E_T(C_{ethanse},2sp^3)$  is purely Coulombic.

The sharing of electrons between two  $C2sp^3$  HOs to form a C-C-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each  $C2sp^3$  HO donates an excess of 25% of its electron density to the C-C-bond MO to form an energy minimum. By considering this electron redistribution in the ethane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{ethame2sp^3}$  of the  $C2sp^3$  shell of ethane may be calculated from the Coulombic energy using Eq.

25 (10.102):

$$r_{ethane2sp^3} = \left(\sum_{n=2}^{5} (Z-n) - 0.25\right) \frac{e^2}{8\pi\varepsilon_0 \left(e151.61569 \, eV\right)} = \frac{9.75e^2}{8\pi\varepsilon_0 \left(e151.61569 \, eV\right)} = 0.87495a_0$$
(14.504)

Using Eqs. (10.102) and (14.504), the Coulombic energy  $E_{Coulomb} \left( C_{ethame}, 2sp^3 \right)$  of the outer electron of the  $C2sp^3$  shell is

$$E_{Coulomb}\left(C_{ethane}, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{ethane2sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.87495a_{0}} = -15.55033 \ eV$$
 (14.505)

During hybridization, one of the spin-paired 2s electrons is promoted to  $C2sp^3$  shell as an 5 unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.505), the energy  $E(C_{elhane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E\left(C_{ethane}, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{ethane2:p^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}} = -15.55033 \ eV + 0.19086 \ eV = -15.35946 \ eV$$

$$(14.506)$$

10 Thus,  $E_T(C-C,2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of the C-C-bond MO is given by the difference between Eq. (14.146) and Eq. (14.506):

$$E_T\left(C - C, 2sp^3\right) = E\left(C_{ethane}, 2sp^3\right) - E\left(C, 2sp^3\right) = -15.35946 \ eV - \left(-14.63489 \ eV\right) = -0.72457 \ eV - \left(-14.63489 \ eV\right) = -0.7247 \ eV - \left(-14.63489 \ eV\right) = -0.7247 \ eV - \left(-14.63489 \ eV\right) = -0.7247 \ eV - \left(-14.$$

Next, consider the formation of the C=C-bond MO of ethylene from two  $CH_2$  15 radicals, each having a  $C2sp^3$  electron with an energy given by Eq. (14.146). The sum  $E_T\left(C_{ethylene},2sp^3\right)$  of calculated energies of  $C2sp^3$ ,  $C^+$ ,  $C^{2+}$ , and  $C^{3+}$  is given by Eq. (14.147). The sharing of electrons between two pairs of  $C2sp^3$  HOs to form a C=C-bond MO permits each participating HO to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating  $C2sp^3$  HO donates an excess of 25% of its electron density to the C=C-bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{ethylene2sp^3}$  of the  $C2sp^3$  shell of ethylene may be calculated from the Coulombic energy using Eqs. (10.102) and (14.147):

$$r_{ethylene2sp^3} = \left(\sum_{n=2}^{5} (Z - n) - 0.5\right) \frac{e^2}{8\pi\varepsilon_0 \left(e151.61569 \, eV\right)}$$

$$= \frac{9.5e^2}{8\pi\varepsilon_0 \left(e151.61569 \, eV\right)}$$

$$= 0.85252a_0$$
(14.508)

where Z=6 for carbon. Using Eqs. (10.102) and (14.508), the Coulombic energy  $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$  of the outer electron of the  $C2sp^3$  shell is

$$E_{Coulomb}\left(C_{ethylene}, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{ethylene2sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.85252a_{0}} = -15.95955 \ eV \tag{14.509}$$

5 During hybridization, one of the spin-paired 2s electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.509), the energy  $E(C_{ethylene}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

$$E\left(C_{ethylene}, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{ethylene2sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}\left(r_{3}\right)^{3}} = -15.95955 \ eV + 0.19086 \ eV = -15.76868 \ eV$$
(14.510)

Thus,  $E_T(C=C,2sp^3)$ , the energy change of each  $C2sp^3$  shell with the formation of the C=C-bond MO is given by the difference between Eq. (14.146) and Eq. (14.510):

$$E_{T}(C = C, 2sp^{3}) = E(C_{ethylene}, 2sp^{3}) - E(C, 2sp^{3})$$

$$= -15.76868 \ eV - (-14.63489 \ eV)$$

$$= -1.13380 \ eV$$
(14.511)

To meet the energy matching condition for all  $\sigma$  MOs at all  $C2sp^3$  HOs, the energy  $E\left(C_{alkane},2sp^3\right)$  of the outer electron of the  $C2sp^3$  shell of each alkane carbon atom must be the average of  $E\left(C_{ethane},2sp^3\right)$  (Eq. (14.506)) and  $E\left(C_{ethylene},2sp^3\right)$  (Eq. (14.510)):

$$E(C_{alkane}, 2sp^{3}) = \frac{E(C_{ethane}, 2sp^{3}) + E(C_{ethylene}, 2sp^{3})}{2}$$

$$= \frac{(-15.35946 \, eV) + (-15.76868 \, eV)}{2}$$

$$= -15.56407 \, eV$$
(14.512)

And,  $E_{T_{albane}}\left(C-C,2sp^3\right)$ , the energy change of each  $C2sp^3$  shell with the formation of each C-C-bond MO, must be the average of  $E_T\left(C-C,2sp^3\right)$  (Eq. (14.507)) and  $E_T\left(C=C,2sp^3\right)$  (Eq. (14.511)):

$$E_{T_{albane}} \left( C - C, 2sp^{3} \right) = \frac{E_{T} \left( C - C, 2sp^{3} \right) + E_{T} \left( C = C, 2sp^{3} \right)}{2}$$

$$= \frac{\left( -0.72457 \, eV \right) + \left( -1.13379 \, eV \right)}{2}$$

$$= -0.92918 \, eV$$
(14.513)

5 Using Eq. (10.102), the radius  $r_{alkane2sp^3}$  of the  $C2sp^3$  shell of each carbon atom of  $C_nH_{2n+2}$  may be calculated from the Coulombic energy using the initial energy  $E_{Coulomb}\left(C,2sp^3\right)=-14.82575\ eV$  (Eq. (14.143)) and  $E_{T_{alkane}}\left(C-C,2sp^3\right)$  Eq. (14.513)), the energy change of each  $C2sp^3$  shell with the formation of each C-C-bond MO. Consider the case of a methyl carbon which donates  $E_{T_{alkane}}\left(C-C,2sp^3\right)$  Eq. (14.513)) to a single 10 C-C bond:

$$r_{alkone2sp^3} = \frac{-e^2}{8\pi\varepsilon_0 \left( E_{Coulomb} \left( C, 2sp^3 \right) + E_{T_{alkone}} \left( C - C, 2sp^3 \right) \right)}$$

$$= \frac{e^2}{8\pi\varepsilon_0 \left( e14.825751 \ eV + e0.92918 \ eV \right)}$$

$$= 0.86359a_0$$
(14.514)

Using Eqs. (10.102) and (14.514), the Coulombic energy  $E_{Coulomb}(C_{alkane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

15 
$$E_{Coulomb}\left(C_{alkane}, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{alkane}^{2}sp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.86359a_{0}} = -15.75493 \ eV \tag{14.515}$$

During hybridization, one of the spin-paired 2s electrons is promoted to  $C2sp^3$  shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.515), the energy  $E(C_{alkane}, 2sp^3)$  of the outer electron of the  $C2sp^3$  shell is

20 
$$E(C_{alkane}, 2sp^3) = \frac{-e^2}{8\pi\varepsilon_0 r_{alkane} r_{alkane} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2(r_3)^3} = -15.75493 \ eV + 0.19086 \ eV = -15.56407 \ eV$$

(14.516)

Thus,  $E_{T_{otherns}}\left(C-C,2sp^3\right)$ , the energy change of each  $C2sp^3$  shell with the formation of each C-C-bond MO is given by the difference between Eq. (14.146) and Eq. (14.516):

$$E_{T_{alkane}}\left(C-C,2sp^{3}\right)=E\left(C_{alkane},2sp^{3}\right)-E\left(C,2sp^{3}\right)=-15.56407\ eV-\left(-14.63489\ eV\right)=-0.92918\ eV$$

$$(14.517)$$

which agrees with Eq. (14.513).

The energy contribution due to the charge donation at each carbon superimposes linearly. In general, the radius  $r_{mol2sp^3}$  of the  $C2sp^3$  HO of a carbon atom of a group of a given molecule is calculated using Eq. (14.514) by considering  $\sum E_{T_{act}} (MO, 2sp^3)$ , the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by

$$r_{mol \, 2sp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(E_{Coulomb} \left(C, 2sp^{3}\right) + \sum E_{T_{mol}} \left(MO, 2sp^{3}\right)\right)}$$

$$= \frac{e^{2}}{8\pi\varepsilon_{0} \left(e14.825751 \ eV + \sum \left|E_{T_{mol}} \left(MO, 2sp^{3}\right)\right|\right)}$$
(14.518)

The  $C2sp^3$  HO of each methyl group of an alkane contributes  $-0.92918\,eV$  to the corresponding single C-C bond; thus, the corresponding  $C2sp^3$  HO radius is given by Eq. 15 (14.514). The  $C2sp^3$  HO of each methylene group of  $C_nH_{2n+2}$  contributes  $-0.92918\,eV$  to each of the two corresponding C-C bond MOs. Thus, the radius of each methylene group of an alkane is given by

$$r_{alkaneC_{methylene} 2sp^3} = \frac{-e^2}{8\pi\varepsilon_0 \left( E_{Cauloinb} \left( C, 2sp^3 \right) + \sum_{T_{alkane}} \left( methylene \ C - C, 2sp^3 \right) \right)}$$

$$= \frac{e^2}{8\pi\varepsilon_0 \left( e14.825751 \ eV + e0.92918 \ eV + e0.92918 \ eV \right)}$$

$$= 0.81549a_0$$
(14.519)

As in the case with ethane, the  $H_2$ -type ellipsoidal MO comprises 75% of the C-C20 bond MO shared between two  $C2sp^3$  HOs corresponding to the electron charge density in
Eq. (11.65) of  $\frac{-0.75e}{2}$ . But, the additional 25% charge-density contribution to the C-Cbond MO causes the electron charge density in Eq. (11.65) to be is given by  $\frac{-e}{2} = -0.5e$ .

Thus, the force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci is given by Eq. (14.152). The distance from the origin of the C-C-bond MO to each focus c' is given by Eq. (14.153). The internuclear distance from is given by Eq. (14.154). The length of the semiminor axis of the prolate spheroidal C-C-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the C-C-bond MO. Since the C-C-bond MO comprises a  $H_2$ -type-ellipsoidal MO that transitions to the  $C_{alkone}2sp^3$  HO of each carbon, the energy  $E\left(C_{alkone},2sp^3\right)$  in Eq. (14.512) adds to that of the  $H_2$ -type ellipsoidal MO to give the total energy of the C-C-bond MO. From the energy equation and the relationship between the axes, the dimensions of the C-C-bond MO are solved. Similarly,  $E\left(C_{alkone},2sp^3\right)$  is added to the energy of the  $H_2$ -type ellipsoidal MO of each C-H bond of the methyl and methylene groups to give their total energy. From the energy equation and the relationship between the axes, the dimensions of the equivalent C-H-bond MOs of the methyl and methylene groups in the alkane are solved.

The general equations for the energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of each C-C-bond MO are the same as those of the CH MO except that energy of the  $C_{alkane}2sp^3$  HO is used. The energy components at each carbon atom superimpose linearly and may be treated independently. Since each prolate spheroidal  $H_2$ -type MO transitions to the  $C_{alkane}2sp^3$  HO of each corresponding carbon of the bond and the energy of the  $C_{alkane}2sp^3$  shell treated independently must remain constant and equal to the  $E(C_{alkane}, 2sp^3)$  given by Eq. (14.512), the total energy  $E'_{T_{alkane}}(C-C,\sigma)$  of the  $\sigma$  component of each C-C-bond MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C_{alkane}2sp^3$  HO and the  $H_2$ -type ellipsoidal MO that forms the  $\sigma$  component of the C-C-bond MO as given by Eq. (14.502) with the electron charge redistribution. The total number of C-C bonds in  $C_nH_{2n+2}$  is n-1. Using Eqs. (13.431) and (14.512),  $E_{T_{alkane}}(C-C,\sigma)$  of the n-1 bonds is given by

$$E_{T_{alkans}}(C-C,\sigma) = (n-1)\left(E_T + E\left(C_{alkans}, 2sp^3\right)\right)$$

$$= (n-1)\left(-\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(0.91771\right)\left(2 - \frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] - 15.56407 \, eV\right)^{(14.520)}$$

To match the boundary condition that the total energy of each  $H_2$ -type ellipsoidal MO is given by Eqs. (11.212) and (13.75),  $E_{T_{ollicity}}$  ( $C-C,\sigma$ ) given by Eq. (14.520) is set equal to (n-1) times Eq. (13.75):

$$E_{T_{alhass}}(C-C,\sigma) = \begin{cases} (n-1)\left(-\frac{e^2}{8\pi\varepsilon_0c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\right) = (n-1)(-31.63536831 \,eV) \end{cases}$$

$$(14.521)$$

From the energy relationship given by Eq. (14.521) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the C-C-bond MO can be solved.

10 Substitution of Eq. (14.153) into Eq. (14.521) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right] = e16.07130$$
(14.522)

The most convenient way to solve Eq. (14.522) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 2.12499a_0 = 1.12450 \times 10^{-10} m \tag{14.523}$$

15 Substitution of Eq. (14.523) into Eq. (14.155) gives

$$c' = 1.45774a_0 = 7.71400 \ X \ 10^{-11} \ m \tag{14.524}$$

The internuclear distance given by multiplying Eq. (14.524) by two is

$$2c' = 2.91547a_0 = 1.54280 X 10^{-10} m (14.525)$$

The experimental C-C bond distance of propane is [3]

$$2c' = 1.532 X 10^{-10} m ag{14.526}$$

The experimental C-C bond distance of butane is [3]

$$2c' = 1.531 \times 10^{-10} m \tag{14.527}$$

Substitution of Eqs. (14.523-14.524) into Eq. (13.62) gives

$$b = c = 1.54616a_0 = 8.18192 \ X \ 10^{-11} \ m \tag{14.528}$$

25 Substitution of Eqs. (14.523-14.524) into Eq. (13.63) gives

$$e = 0.68600 \tag{14.529}$$

The nucleus of the C atoms comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{alkane}2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta^1$  is given by Eq. (13.261) where for methylene bonds  $r_n = r_{alkane2sp^3} = r_{methylene2sp^3} = 0.81549a_0$  is the radius of the  $C_{alkane}2sp^3$  shell given by Eq. (14.519). Substitution of Eqs. (14.523-14.524) into Eq. (13.261) gives

$$\theta' = 56.41^{\circ}$$
 (14.530)

Then, the angle  $\theta_{C-C_{\text{offerms}}2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear

10 axis is

$$\theta_{C-C......2sp^3HO} = 180^{\circ} - 56.41^{\circ} = 123.59^{\circ}$$
 (14.531)

as shown in Figure 48.

15 Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-C_{alkons},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{alkons}2sp^3$  radial vector obeys the following relationship:

$$r_{alkane2sp}$$
,  $\sin \theta_{C-C_{anac}2sp^3HO} = 0.81549a_0 \sin \theta_{C-C_{anac}2sp^3HO} = b \sin \theta_{C-C_{alkane},H_2MO}$  (14.532)

20 such that

$$\theta_{C-C_{alknow}, H_2MO} = \sin^{-1} \frac{0.81549a_0 \sin \theta_{C-C_{alknow}} 2sp^3 HO}{b} = \sin^{-1} \frac{0.81549a_0 \sin 123.59^{\circ}}{b}$$
(14.533)

with the use of Eq. (14.531). Substitution of Eq. (14.528) into Eq. (14.533) gives

$$\theta_{C-C_{con},H_{c}MO} = 26.06^{\circ}$$
 (14.534)

Then, the distance  $d_{C-C_{allow},H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-C_{alkone}, H_2MO} = a\cos\theta_{C-C_{alkone}, H_2MO}$$
 (14.535)

Substitution of Eqs. (14.523) and (14.534) into Eq. (14.535) gives

$$d_{C-C_{-local},H,MO} = 1.90890a_0 = 1.01015 X 10^{-10} m$$
 (14.536)

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The distance  $d_{C-C_{alkma}} 2sp^3HO$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-C_{climat}, 2sp^3HO} = d_{C-C_{climat}, H_2MO} - c'$$
 (14.537)

Substitution of Eqs. (14.524) and (14.536) into Eq. (14.537) gives

$$d_{C-C_{alknew}} 2sp^{3}HO = 0.45117a_{0} = 2.38748 \times 10^{-11} m$$
 (14.538)

# FORCE BALANCE OF THE CH<sub>3</sub> MOs OF CONTINUOUS-CHAIN ALKANES

Each of the two  $CH_3$  MOs must comprise three equivalent C-H bonds with each 10 comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO as given by Eq. (13.540):

$$3\left[1 C2sp^{3} + 0.75 H_{2} MO\right] \rightarrow CH_{3} MO \tag{14.539}$$

The force balance of the  $CH_3$  MO is determined by the boundary conditions that arise from 15 the linear combination of orbitals according to Eq. (14.539) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH_3$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each C-H-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each C-H-bond MO. Since each of the three prolate spheroidal C-H-bond MOs comprises an  $H_2$ -type-ellipsoidal MO that transitions to the  $C_{alkone} 2sp^3$  HO of  $C_nH_{2n+2}$ , the energy  $E\left(C_{alkone}, 2sp^3\right)$  of Eq. (14.512) adds to that of the three corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_3$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_3$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ , T, and  $V_m$  are the same as those of methyl radical, three times those of CH corresponding to the three C-H bonds except that energy of the  $C_{alkane}2sp^3$  HO is used. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C_{alkane}2sp^3$  HO and the energy of the  $C_{alkane}2sp^3$  shell must remain constant and equal to the  $E\left(C_{alkane},2sp^3\right)$  given by Eq. (14.512), the total energy  $E_{T_{alkane}}\left(CH_3\right)$  of the  $CH_3$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C_{alkane}2sp^3$  HO and the three  $H_2$ -type ellipsoidal MOs that forms the  $CH_3$  MO as given by Eq. (14.539). Using Eq. (13.431) or Eq. (13.541),  $E_{T_{alkane}}\left(CH_3\right)$  is given by

$$E_{T_{alkans}}(CH_3) = E_T + E(C_{alkans}, 2sp^3)$$

$$= -\frac{3e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 15.56407 \ eV$$
(14.540)

 $E_{T_{allows}}$  (CH<sub>3</sub>) given by Eq. (14.540) is set equal to three times the energy of the  $H_2$ -type ellipsoidal MO minus two times the Coulombic energy of H given by Eq. (13.542):

$$E_{T}(CH_{3}) = -\frac{3e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \ eV = -67.69450 \ eV$$
(14.541)

15 From the energy relationship given by Eq. (14.541) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH<sub>3</sub> MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.541) gives

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e52.13044$$
 (14.542)

The most convenient way to solve Eq. (14.542) is by the reiterative technique using a 20 computer. The result to within the round-off error with five-significant figures is

$$a = 1.64920a_0 = 8.72720 \ X \ 10^{-11} \ m \tag{14.543}$$

Substitution of Eq. (14.543) into Eq. (14.60) gives

$$c' = 1.04856a_0 = 5.54872 \ X \ 10^{-11} \ m \tag{14.544}$$

The internuclear distance given by multiplying Eq. (14.544) by two is

$$2c' = 2.09711a_0 = 1.10974 \times 10^{-10} m \tag{14.545}$$

The experimental C-H bond distance of propane is [3]

$$2c' = 1.107 X 10^{-10} m ag{14.546}$$

Substitution of Eqs. (14.543-14.544) into Eq. (14.62) gives

$$b = c = 1.27295a_0 = 6.73616 \times 10^{-11} m \tag{14.547}$$

5 Substitution of Eqs. (14.543-14.544) into Eq. (14.63) gives

$$e = 0.63580 \tag{14.548}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{alkane}2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270).

10 The polar intersection angle  $\theta'$  is given by Eq. (13.261) where  $r_n = r_{alkane2sp^3} = 0.86359a_0$  is the radius of the  $C_{alkane}2sp^3$  shell. Substitution of Eqs. (14.543-14.544) into Eq. (13.261) gives

$$\theta' = 77.49^{\circ}$$
 (14.549)

Then, the angle  $\theta_{C-H_{allow}2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear 15 axis is

$$\theta_{C-H_{alkowe} 2sp^3HO} = 180^{\circ} - 77.49^{\circ} = 102.51^{\circ}$$
 (14.550)

as shown in Figure 49.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{altons}, H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{alkane} 2sp^3$  radial vector obeys the following relationship:

$$r_{alkane2sp^3} \sin \theta_{C-H_{alkone}2sp^3HO} = 0.86359a_0 \sin \theta_{C-H_{alkone}2sp^3HO} = b \sin \theta_{C-H_{alkone},H_2MO}$$
 (14.551)

25 such that

$$\theta_{C-H_{alknow},H_2MO} = \sin^{-1} \frac{0.86359a_0 \sin \theta_{C-H_{alknow}2.sp^3HO}}{b} = \sin^{-1} \frac{0.86359a_0 \sin 102.51^{\circ}}{b} \quad (14.552)$$

with the use of Eq. (14.550). Substitution of Eq. (14.547) into Eq. (14.552) gives

$$\theta_{C-H_{alkmin},H_2MO} = 41.48^{\circ} \tag{14.553}$$

Then, the distance  $d_{C-H_{alkars},H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{-hoss},H_{2}MO} = a\cos\theta_{C-H_{-hoss},H_{2}MO} \tag{14.554}$$

Substitution of Eqs. (14.543) and (14.553) into Eq. (14.554) gives

$$d_{C-H_{about},H,MO} = 1.23564a_0 = 6.53871 \times 10^{-11} m$$
 (14.555)

The distance  $d_{C-H_{elbons}2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{about}, H_2bHO} = d_{C-H_{abbut}, H_2bHO} - c' (14.556)$$

Substitution of Eqs. (14.544) and (14.555) into Eq. (14.556) gives

$$d_{C-H_{\text{obsym}}2:p^3HO} = 0.18708a_0 = 9.89999 X 10^{-12} m$$
 (14.557)

## BOND ANGLE OF THE CH, AND CH, GROUPS

Each  $CH_3$  MO comprises a linear combination of three C-H-bond MOs. Each C-H-bond MO comprises the superposition of a  $H_2$ -type ellipsoidal MO and the  $C_{alkane}2sp^3$  HO.

15 A bond is also possible between the two H atoms of the C-H bonds. Such H-H bonding would decrease the C-H bond strength since electron density would be shifted from the C-H bonds to the H-H bond. Thus, the bond angle between the two C-H bonds is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal H atoms of the C-H bonds is zero. From Eqs. (11.79) and (13.228), the distance 20 from the origin to each focus of the H-H ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{14.558}$$

The internuclear distance from Eq. (14.558) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.559}$$

The length of the semiminor axis of the prolate spheroidal H-H MO b=c is given by Eq. 25 (14.62).

The bond angle of the  $CH_3$  groups of  $C_nH_{2n+2}$  is derived by using the orbital composition and an energy matching factor as in the case with the  $CH_3$  radical. Since each pair of  $H_2$ -type ellipsoidal MOs initially comprise 75% of the H electron density of  $H_2$  and

the energy of each  $H_2$ -type ellipsoidal MO is matched to that of the  $C_{alkane}2sp^3$  HO, the component energies and the total energy  $E_T$  of the H-H bond are given by Eqs. (13.67-13.73) except that  $V_e$ , T, and  $V_m$  are corrected for the hybridization-energy-matching factor of 0.86359. Hybridization with 25% electron donation to the C-C-bond gives rise to the  $C_{alkane}2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}\left(C_{alkane},2sp^3\right)$  given by Eq. (14.515). The corresponding normalization factor for determining the zero of the total H-H bond energy is given by the ratio of 15.75493 eV, the magnitude of  $E_{Coulomb}\left(C_{alkane},2sp^3\right)$  given by Eq. (14.515), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The hybridization energy factor  $C_{alkane}2sp^3HO$  is

$$C_{alkaneC2sp^3HO} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{alkane2sp^3}}} = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.86359 a_0}} = \frac{13.605804 \, eV}{15.75493 \, eV} = 0.86359 \quad (14.560)$$

Substitution of Eq. (14.558) into Eq. (13.233) with the hybridization factor of 0.86359 gives

9 gives
$$0 = \begin{bmatrix} \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left[ (0.86359)^{-1} \left( \frac{3}{2} - \frac{3}{8} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 a^3}}}{\frac{m_e}{m_e c^2}}} \right] \\ + \hbar\sqrt{\frac{0.75e^2}{8\pi\varepsilon_0 a^3} \frac{e^2}{8\pi\varepsilon_0 (a + c')^3}} \\ 0.5m_p$$

15 From the energy relationship given by Eq. (14.561) and the relationship between the axes given by Eqs. (14.558-14.559) and (14.62-14.63), the dimensions of the H-H MO can be solved.

The most convenient way to solve Eq. (14.561) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$20 a = 5.8660a_0 = 3.1042 X 10^{-10} m (14.562)$$

Substitution of Eq. (14.562) into Eq. (14.558) gives

(14.561)

$$c' = 1.7126a_0 = 9.0627 \ X \ 10^{-11} \ m \tag{14.563}$$

419

The internuclear distance given by multiplying Eq. (14.563) by two is

$$2c' = 3.4252a_0 = 1.8125 \ X \ 10^{-10} \ m \tag{14.564}$$

Substitution of Eqs. (14.562-14.563) into Eq. (14.62) gives

$$b = c = 5.6104a_0 = 2.9689 X 10^{-10} m ag{14.565}$$

5 Substitution of Eqs. (14.562-14.563) into Eq. (14.63) gives

$$e = 0.2920 \tag{14.566}$$

Using  $2c'_{H-H}$  (Eq. (14.564)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (14.561)), and  $2c'_{C-H}$ , the internuclear distance of each C-H bond, the corresponding bond angle can be determined from the law of cosines. Since the internuclear distance of each C-H bond of  $CH_3$  (Eq. (14.545)) and  $CH_2$  (Eq. (14.597)) are sufficiently equivalent, the bond angle determined with either is within experimental error of being the same. Using, Eqs. (13.242), (14.545), and (14.564), the bond angle  $\theta$  between the C-H bonds is

$$\theta = \cos^{-1}\left(\frac{2(2.09711)^2 - (3.4252)^2}{2(2.09711)^2}\right) = \cos^{-1}\left(-0.33383\right) = 109.50^{\circ}$$
 (14.567)

15 The experimental angle between the C-H bonds is [19]

$$\theta = 109.3^{\circ}$$
 (14.568)

The  $CH_3$  radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance  $d_{origin-H}$  from the origin to the nucleus of a hydrogen atom given by Eqs. (14.564) and (13.412) is

$$20 d_{origin-H} = 1.97754a_0 (14.569)$$

The height along the z-axis of the pyramid from the origin to C nucleus  $d_{leight}$  given by Eqs. (13.414), (14.545), and (14.569) is

$$d_{height} = 0.69800a_0 \tag{14.570}$$

The angle  $\theta_v$  of each C-H bond from the z-axis given by Eqs. (13.416), (14.569), and 25 (14.570) is

$$\theta_{y} = 70.56^{\circ}$$
 (14.571)

The C-C bond is along the z-axis. Thus, the bond angle  $\theta_{C-C-H}$  between the internuclear axis of the C-C bond and a H atom of the methyl groups is given by

$$\theta_{C-C-H} = 180 - \theta_{v} \tag{14.572}$$

Substitution of Eq. (14.571) into Eq. (14.572) gives

$$\theta_{C-C-H} = 109.44^{\circ}$$
 (14.573)

The experimental angle between the C-C-H bonds is [19]

$$\theta_{C-C-H} = 109.3^{\circ}$$
 (14.574)

5 The  $C_nH_{2n+2}$  MOs shown in Figures 50-60 were rendered using these parameters. A minimum energy is obtained with a staggered configuration consistent with observations [3].

#### ENERGIES OF THE CH, GROUPS

The energies of each  $CH_3$  group of  $C_nH_{2n+2}$  are given by the substitution of the semiprincipal axes (Eqs. (14.543-14.544) and (14.547)) into the energy equations of methyl radical (Eqs. (13.556-13.560)), with the exception that  $E(C_{alkane}, 2sp^3)$  (Eq. (14.514)) replaces  $E(C, 2sp^3)$  in Eq. (13.560):

$$V_e = 3(0.91771) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -107.32728 \ eV$$
 (14.575)

$$V_p = \frac{3e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 38.92728 \ eV \tag{14.576}$$

5 
$$T = 3(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 32.53914 \text{ eV}$$
 (14.577)

$$V_{m} = 3(0.91771) \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} = -16.26957 \ eV$$
 (14.578)

$$E_{T_{albane}}(CH_3) = \begin{pmatrix} -\frac{3e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \\ -15.56407 \ eV \end{pmatrix} = -67.69451 \ eV$$
 (14.579)

where  $E_{T_{class}}$  (CH<sub>3</sub>) is given by Eq. (14.540) which is reiteratively matched to Eq. (13.542) within five-significant-figure round off error.

## VIBRATION OF THE 12CH<sub>3</sub> GROUPS

20

The vibrational energy levels of the C-H bonds of  $CH_3$  in  $C_nH_{2n+2}$  may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived

from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

#### THE DOPPLER ENERGY TERMS OF THE 12CH, GROUPS

5 The equations of the radiation reaction force of the methyl groups in  $C_nH_{2n+2}$  are the same as those of the methyl radical with the substitution of the methyl-group parameters. Using Eq. (13.561), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}} = 2.49286 \, X \, 10^{16} \, rad/s \tag{14.580}$$

where b is given by Eq. (14.547). The kinetic energy,  $E_K$ , is given by Planck's equation 10 (Eq. (11.127)):

$$\overline{E}_{\kappa} = \hbar \omega = \hbar 2.49286 \, X \, 10^{16} \, rad \, / \, s = 16.40846 \, eV$$
 (14.581)

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.581) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the 15 three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537 \ eV \sqrt{\frac{2e(16.40846 \ eV)}{m_e c^2}} = -0.25352 \ eV \tag{14.582}$$

$$\overline{E}'_{alkane\ osc}\left(^{12}CH_{3}\right) = \overline{E}_{D} + \overline{E}_{Kvib} = \overline{E}_{D} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(14.583)

25 
$$\overline{E}'_{alkane\ osc} (^{12}CH_3) = -0.25352\ eV + \frac{1}{2} (0.35532\ eV) = -0.07586\ eV$$
 (14.584)

Given that the vibration and reentrant oscillation is for three C-H bonds,  $\overline{E}_{alkane\ asc}\left(^{12}CH_3\right)$ , is:

$$\overline{E}_{alkane \ osc} \left( ^{12}CH_3 \right) = 3 \left( \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) 
= 3 \left( -0.25352 \ eV + \frac{1}{2} \left( 0.35532 \ eV \right) \right) 
= -0.22757 \ eV$$
(14.585)

## 5 TOTAL BOND ENERGIES OF THE 12CH<sub>3</sub> GROUPS

 $E_{alkameT+osc}(^{12}CH_3)$ , the total energy of each  $^{12}CH_3$  group including the Doppler term, is given by the sum of  $E_{T_{alkame}}(CH_3)$  (Eq. (14.579)) and  $\overline{E}_{alkame\ osc}(^{12}CH_3)$  given by Eq. (14.585):

$$E_{alkaneT+osc}\left(CH_{3}\right) = V_{e} + T + V_{m} + V_{p} + E\left(C_{alkane}, 2sp^{3}\right) + \overline{E}_{alkane\ osc}\left(^{12}CH_{3}\right)$$

$$= E_{T_{elkane}}\left(CH_{3}\right) + \overline{E}_{alkane\ osc}\left(^{12}CH_{3}\right)$$
(14.586)

$$E_{alkaneT+osc} \binom{12CH_3}{eV} = \begin{cases} \left(0.91771\right) \left(2 - \frac{1}{2} \frac{a_0}{a}\right) \ln \frac{a+c'}{a-c'} - 1\right] - 15.56407 \ eV \end{cases}$$

$$= -67.69450 \ eV - 3 \left(0.25352 \ eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}\right)$$

(14.587)

From Eqs. (14.585-14.587), the total energy of each  $^{12}CH_3$  is

$$E_{alkaneT+osc} {1^{2}CH_{3}} = -67.69450 \ eV + \overline{E}_{alkane \ osc} {1^{2}CH_{3}}$$

$$= -67.69450 \ eV - 3 \left( 0.25352 \ eV - \frac{1}{2} (0.35532 \ eV) \right)$$

$$= -67.92207 \ eV$$
(14.588)

where  $\omega_e$  given by Eq. (13,458) was used for the  $\hbar\sqrt{\frac{k}{\mu}}$  term.

10

The total  $CH_3$  bond dissociation energy,  $E_{D_{alkane}}(^{12}CH_3)$  is given by the sum of the initial  $C2sp^3$  HO energy,  $E(C,2sp^3)$  (Eq. (14.146)), and three times the energy of the hydrogen atom,  $E_D(H)$  (Eq. (13.154)), minus  $E_{alkaneT+asc}(^{12}CH_3)$  (Eq. (14.588)):

$$E_{D_{alkone}T}(^{12}CH_3) = E(C, 2sp^3) + 3E(H) - E_{alkone}T + osc(^{12}CH_3)$$
(14.589)

5 Thus, the total  $^{12}CH_3$  bond dissociation energy,  $E_{D_{alkmr}}\left(^{12}CH_3\right)$  is

$$E_{D_{elhors}} {\binom{12}{CH_3}} = -(14.63489 \ eV + 3(13.59844 \ eV)) - (E_{alkaneT+osc} {\binom{12}{CH_2}})$$

$$= -55.43021 \ eV - (-67.92207 \ eV)$$

$$= 12.49186 \ eV$$
(14.590)

# FORCE BALANCE OF THE CH<sub>2</sub> MOs OF CONTINUOUS-CHAIN ALKANES

10 Each of the  $CH_2$  MOs must comprise two equivalent C-H bonds with each comprising 75% of a  $H_2$ -type ellipsoidal MO and a  $C2sp^3$  HO as given by Eq. (13.494):

$$2\left[1 C2sp^{3} + 0.75 H_{2} MO\right] \rightarrow CH_{2} MO \tag{14.591}$$

15 The force balance of each  $CH_2$  MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.591) and the energy matching condition between the hydrogen and  $C2sp^3$  HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each  $H_2$ -type-ellipsoidal-MO component of the  $CH_2$  MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each C-H-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal C-H-bond MO b=c is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each C-H-bond MO. Since each of the two prolate spheroidal C-H-bond MOs comprises an  $H_2$ -type-ellipsoidal MO that transitions to the  $C_{alkane}2sp^3$  HO of  $C_nH_{2n+2}$ , the energy  $E(C_{alkane},2sp^3)$ 

of Eq. (14.512) adds to that of the two corresponding  $H_2$ -type ellipsoidal MOs to give the total energy of the  $CH_2$  MO. From the energy equation and the relationship between the axes, the dimensions of the  $CH_2$  MO are solved.

The energy components of  $V_e$ ,  $V_p$ , T, and  $V_m$  are the same as those of dihydrogen carbide radical, two times those of CH corresponding to the two C-H bonds except that energy of the  $C_{alkane} 2sp^3$  HO is used. Since the each prolate spheroidal  $H_2$ -type MO transitions to the  $C_{alkane} 2sp^3$  HO and the energy of the  $C_{alkane} 2sp^3$  shell treated independently must remain constant and equal to the  $E(C_{alkane}, 2sp^3)$  given by Eq. (14.512), the total energy  $E_{T_{alkane}}(CH_2)$  of the  $CH_2$  MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the  $C_{alkane} 2sp^3$  HO and the two  $H_2$ -type ellipsoidal MOs that forms the  $CH_2$  MO as given by Eq. (14.591). Using Eq. (13.431) or Eq. (13.495),  $E_{T_{alkane}}(CH_2)$  is given by

$$E_{T_{alkane}}(CH_2) = E_T + E(C_{alkane}, 2sp^3)$$

$$= -\frac{2e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 eV$$
(14.592)

 $E_{T_{absol}}(CH_2)$  given by Eq. (14.592) is set equal to two times the energy of the  $H_2$ -type 15 ellipsoidal MO minus the Coulombic energy of H given by Eq. (13.496):

$$E_{T}(CH_{2}) = -\frac{2e^{2}}{8\pi\varepsilon_{0}c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \ eV = -49.66493 \ eV$$
(14.593)

From the energy relationship given by Eq. (14.593) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the  $CH_2$  MO can be solved.

20 Substitution of Eq. (13.60) into Eq. (14.593) gives

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e34.10086$$
 (14.594)

The most convenient way to solve Eq. (14.594) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.67122a_0 = 8.84370 \ X \ 10^{-11} \ m \tag{14.595}$$

Substitution of Eq. (14.595) into Eq. (14.60) gives

$$c' = 1.05553a_0 = 5.58563 \times 10^{-11} m \tag{14.596}$$

The internuclear distance given by multiplying Eq. (14.596) by two is

$$2c' = 2.11106a_0 = 1.11713 X 10^{-10} m (14.597)$$

5 The experimental C-H bond distance of butane is [3]

$$2c' = 1.117 X 10^{-10} m ag{14.598}$$

Substitution of Eqs. (14.595-14.596) into Eq. (14.62) gives

$$b = c = 1.29569a_0 = 6.85652 X 10^{-11} m ag{14.599}$$

Substitution of Eqs. (14.595-14.596) into Eq. (14.63) gives

$$10 e = 0.63159 (14.600)$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each  $H_2$ -type ellipsoidal MO. The parameters of the point of intersection of the  $H_2$ -type ellipsoidal MO and the  $C_{alkane}2sp^3$  HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle  $\theta$ ' is given by Eq. (13.261) where  $r_n = r_{methylene2sp^3} = 0.81549a_0$  is

15 the radius of the  $C_{methylene} 2sp^3$  shell (Eq. (14.521)). Substitution of Eqs. (14.595-14.596) into Eq. (13.261) gives

$$\theta' = 68.47^{\circ}$$
 (14.601)

Then, the angle  $\theta_{C-H_{elban},2sp^3HO}$  the radial vector of the  $C2sp^3$  HO makes with the internuclear axis is

20 
$$\theta_{C-H_{affrom}} = 180^{\circ} - 68.47^{\circ} = 111.53^{\circ}$$
 (14.602)

as shown in Figure 49. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle  $\omega t = \theta_{C-H_{alkow},H_2MO}$  between the internuclear axis and the point of intersection of the  $H_2$ -type ellipsoidal MO with the  $C_{alkow}2sp^3$  radial vector obeys the following relationship:

25 
$$r_{alkane 2sp^3} \sin \theta_{C-H_{alkane 2sp^3HO}} = 0.81549 a_0 \sin \theta_{C-H_{alkane 2sp^3HO}} = b \sin \theta_{C-H_{alkane 1}, H_2MO}$$
 (14.603)

such that

$$\theta_{C-H_{others},H_2MO} = \sin^{-1} \frac{0.81549a_0 \sin \theta_{C-H_{others},25p^3HO}}{b} = \sin^{-1} \frac{0.81549a_0 \sin 111.53^{\circ}}{b} \quad (14.604)$$

with the use of Eq. (14.602). Substitution of Eq. (14.599) into Eq. (14.604) gives

$$\theta_{C-H_{alkam},H_2MO} = 35.84^{\circ}$$
 (14.605)

Then, the distance  $d_{C-H_{atham},H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{about},H_{2}MO} = a\cos\theta_{C-H_{about},H_{2}MO} \tag{14.606}$$

Substitution of Eqs. (14.595) and (14.605) into Eq. (14.606) gives

5 
$$d_{C-H_{alkans},H_2MO} = 1.35486a_0 = 7.16963 \ X \ 10^{-11} \ m \tag{14.607}$$

The distance  $d_{C-H_{alkow}2sp^3HO}$  along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{about}, 2sp^3HO} = d_{C-H_{about}, H_2MO} - c' (14.608)$$

Substitution of Eqs. (14.596) and (14.605) into Eq. (14.608) gives

$$d_{C-H_{obser}2sp^3HO} = 0.29933a_0 = 1.58400 X 10^{-11} m$$
 (14.609)

The charge-density in each C-C-bond MO is increased by a factor of 0.25 with the formation of the  $C_{alkane} 2sp^3$  HOs each having a smaller radius. Using the orbital composition of the C-C-bond MOs (Eq. (14.504),  $CH_3$  groups (Eq. (14.539)), and the  $CH_2$  groups (Eq. (14.591)), the radii of  $C1s = 0.17113a_0$  (Eq. (10.51)),  $C_{alkane}2sp^3 = 0.86359a_0$  (Eq. (14.514)), 15 and  $C_{alkane} 2sp^3 = C_{methodene} 2sp^3 = 0.81549a_0$  (Eq. (14.521)) shells, the parameters of the C-C-bonds (Eqs. (13.3-13.4), (14.523-14.525), and (14.528-14.538)), the parameters of the C-H-bond MOs of the  $CH_3$  groups (Eqs. (13.3-13.4), (14.544-14.545), and (14.547-14.557)), the parameters of the C-H-bond MOs of the  $CH_2$  groups (Eqs. (13.3-13.4), (14.595-14.597), and (14.599-14.609)), and the bond-angle parameters (Eqs. (14.562-20 14.574)), the charge-density of the  $C_n H_{2n+2}$  MO comprising the linear combination 2n+2C-H-bond MOs and n-1 C-C-bond MOs, each bridging one or more methyl or methylene groups is shown for representative cases where data was available [17-18]. Propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane are shown in Figures 50-60, respectively. Each C-H-bond MO comprises a 25  $H_2$ -type ellipsoidal MO and a  $C_{olkane}2sp^3$  HO having the dimensional diagram shown in Figure 48. Each C-C-bond MO comprises a  $H_2$ -type ellipsoidal MO bridging two  $C_{\text{others}} 2sp^3$  HOs having the dimensional diagram shown in Figure 49.

#### ENERGIES OF THE CH<sub>2</sub> GROUPS

The energies of each  $CH_2$  group of  $C_nH_{2n+2}$  are given by the substitution of the semiprincipal axes (Eqs. (14.595-14.596) and (14.599)) into the energy equations of dihydrogen carbide radical (Eqs. (13.510-13.514)), with the exception that  $E\left(C_{alkane}, 2sp^3\right)$ 

5 (Eq. (14.512)) replaces  $E(C, 2sp^3)$  in Eq. (13.514):

$$V_e = 2(0.91771) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -70.41425 \ eV$$
 (14.610)

$$V_p = \frac{2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} = 25.78002 \, eV \tag{14.611}$$

$$T = 2(0.91771) \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 21.06675 \ eV$$
 (14.612)

$$V_m = 2(0.91771) \frac{-\hbar^2}{4m \cdot a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -10.53337 \text{ eV}$$
 (14.613)

10 
$$E_{T_{alkner}}(CH_2) = -\frac{2e^2}{8\pi\varepsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] - 15.56407 \ eV = -49.66493 \ eV$$
 (14.614)

where  $E_{T_{alterne}}$  (CH<sub>2</sub>) is given by Eq. (14.592) which is reiteratively matched to Eq. (13.496) within five-significant-figure round off error.

## 15 VIBRATION OF THE 12CH2 GROUPS

The vibrational energy levels of the C-H bonds of  $CH_2$  in  $C_nH_{2n+2}$  may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section 20 and the Vibration of Hydrogen-Type Molecules section.

## THE DOPPLER ENERGY TERMS OF THE 12CH2 GROUPS

The equations of the radiation reaction force of the methylene groups in  $C_nH_{2n+2}$  are the same as those of the dihydrogen carbide radical with the substitution of the methylene-group

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parameters. Using Eq. (13.515), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{\frac{4\pi\varepsilon_0 b^3}{m_e}}} = 2.42751 \times 10^{16} \text{ rad/s}$$
 (14.615)

where b is given by Eq. (14.599). The kinetic energy,  $E_K$ , is given by Planck's equation 5 (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.42751 \, X \, 10^{16} \, rad/s = 15.97831 \, eV$$
 (14.616)

In Eq. (11.181), substitution of  $E_T(H_2)$  (Eqs. (11.212) and (13.75)), the maximum total energy of each  $H_2$ -type MO, for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.616) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the 10 three bonds for the reentrant orbit:

$$\overline{E}_{D} \cong E_{hv} \sqrt{\frac{2\overline{E}_{K}}{Mc^{2}}} = -31.63537 \ eV \sqrt{\frac{2e(15.97831 \ eV)}{m_{e}c^{2}}} = -0.25017 \ eV$$
 (14.617)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of  $CH_2$  due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{osc}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (14.617) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each C-H bond. Using  $\omega_e$  given by Eq. (13.458) for  $\overline{E}_{Kvib}$  of the transition state having two independent bonds,  $\overline{E}_{alkane\ osc}^{'}\binom{12}{CH_2}$  per bond is

$$\overline{E}'_{alkane\ osc}\left(^{12}CH_{2}\right) = \overline{E}_{D} + \overline{E}_{Kvib} = \overline{E}_{D} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
(14.618)

20 
$$\bar{E}'_{alkane\ osc}(^{12}CH_2) = -0.25017\ eV + \frac{1}{2}(0.35532\ eV) = -0.07251\ eV$$
 (14.619)

Given that the vibration and reentrant oscillation is for two C-H bonds,  $\overline{E}_{alkane\ osc}(^{12}CH_2)$ , is:

$$\overline{E}_{alkane \ osc} \left(^{12}CH_2\right) = 2 \left(\overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}\right) = 2 \left(-0.25017 \ eV + \frac{1}{2} \left(0.35532 \ eV\right)\right) = -0.14502 \ eV$$

(14.620)

## TOTAL BOND ENERGIES OF THE 12CH, GROUPS

 $E_{alkaneT+osc}(^{12}CH_2)$ , the total energy of each  $^{12}CH_2$  group including the Doppler term, is given 5 by the sum of  $E_{T_{alkane}}(CH_2)$  (Eq. (14.614)) and  $\overline{E}_{alkane\ osc}(^{12}CH_2)$  given by Eq. (14.620):

$$\begin{split} E_{alkaneT+ose}\left(CH_{2}\right) &= V_{e} + T + V_{m} + V_{p} + E\left(C_{alkane}, 2sp^{3}\right) + \overline{E}_{alkane\ ose}\left(^{12}CH_{2}\right) \\ &= E_{T_{alkane}}\left(CH_{2}\right) + \overline{E}_{alkane\ ose}\left(^{12}CH_{2}\right) \end{split} \tag{14.621}$$

$$E_{alkameT+osc} \binom{^{12}CH_2}{=} \left\{ \begin{pmatrix} \frac{-2e^2}{8\pi\varepsilon_0c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \ eV \right) \\ -2 \left( (31.63536831 \ eV) \sqrt{\frac{\frac{3}{4} \frac{e^2}{4\pi\varepsilon_0b^3}}{\frac{m_e}{m_ec^2}} - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}} \right) \\ = -49.66493 \ eV - 2 \left( 0.25017 \ eV - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$

(14.622)

From Eqs. (14.620-14.622), the total energy of each  $^{12}CH_2$  is

$$E_{alkaneT+osc} \left(^{12}CH_{2}\right) = -49.66493 \ eV + \overline{E}_{alkane \ osc} \left(^{12}CH_{2}\right)$$

$$= -49.66493 \ eV - 2\left(0.25017 \ eV - \frac{1}{2}(0.35532 \ eV)\right)$$

$$= -49.80996 \ eV$$
(14.623)

where  $\omega_e$  given by Eq. (13.458) was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

The derivation of the total  $CH_2$  bond dissociation energy,  $E_{D_{alhows}}(^{12}CH_2)$  follows from that of the bond dissociation energy of dihydrogen carbide radical,  $E_D(^{12}CH_2)$ , given by Eqs. (13.524-13.527).  $E_{D_{alhows}}(^{12}CH_2)$  is given by the sum of the initial  $C2sp^3$  HO energy, 15  $E(C,2sp^3)$  (Eq. (14.146)), and two times the energy of the hydrogen atom, E(H) (Eq. (13.154)), minus the sum of  $E_{alkaneT+osc}(^{12}CH_2)$  (Eq. (14.623)) and E(magnetic) (Eq. 13.524)):

$$E_{D_{alkane}T+osc} \binom{12}{CH_2} = E(C, 2sp^3) + 2E(H) - E_{alkaneT+osc} \binom{12}{CH_2} - E(magnetic)$$
 (14.624)

Thus, the total  $^{12}CH_2$  bond dissociation energy,  $E_{D_{othern}}\left(^{12}CH_2\right)$  is

$$E_{D_{alkane}} \left( ^{12}CH_{2} \right) = -\left( 14.63489 \ eV + 2\left( 13.59844 \ eV \right) \right) - \left( E_{alkane} \left( ^{12}CH_{2} \right) + E\left( magnetic \right) \right)$$

$$= -41.83177 \ eV - \left( -49.80996 \ eV + 0.14803 \ eV \right)$$

$$= 7.83016 \ eV$$

(14.625)

5

## SUM OF THE ENERGIES OF THE C-C $\sigma$ MOs AND THE HOs OF CONTINUOUS-CHAIN ALKANES

The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  of the C-C-bond MOs are the same as those of the CH MO except that energy of the  $C_{alkane}2sp^3$  HO is used. The energies of each C-C-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.523-14.524) and (14.528)) into the energy equations of the CH MO (Eqs. (13.449-13.453)), with the exception that  $E\left(C_{alkane}, 2sp^3\right)$  (Eq. (14.512)) replaces  $E\left(C, 2sp^3\right)$  in Eq. (13.453). The total number of C-C bonds of  $C_nH_{2n+2}$  is n-1. Thus, the energies of the n-1 bonds is given by

15 
$$V_e = (n-1)(0.91771) \frac{-2e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -(n-1)28.79214 \, eV \quad (14.626)$$

$$V_{p} = \frac{(n-1)e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2}-b^{2}}} = (n-1)9.33352 \ eV$$
 (14.627)

$$T = (n-1)(0.91771) \frac{\hbar^2}{2m_a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = (n-1)6.77464 \text{ eV}$$
 (14.628)

$$V_m = (n-1)(0.91771) \frac{-\hbar^2}{4m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -(n-1)3.38732 \, eV \qquad (14.629)$$

$$E_{T_{almost}}(C-C,\sigma) = -\frac{(n-1)e^2}{8\pi\epsilon_0 c'} \left[ (0.91771) \left( 2 - \frac{1}{2} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] - 15.56407 \ eV$$
$$= -(n-1)31.63537 \ eV$$

20

(14.630)

where  $E_{T_{altans}}(C-C,\sigma)$  is the total energy of the C-C  $\sigma$  MOs given by Eq. (14.520) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

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Since there are two carbon atoms per bond, the number of C-C bonds is n-1, and the energy change of each  $C2sp^3$  shell due to the decrease in radius with the formation of each C-C-bond MO is  $E_{T_{alkness}}\left(C-C,2sp^3\right)$  (Eq. (14.517)), the total energy of the C-C-bond MOs,  $E_{T_{alkness}}\left(C-C\right)$ , is given by the sum of  $2(n-1)E_{T_{alkness}}\left(C-C,2sp^3\right)$  and  $E_{T_{alkness}}\left(C-C,\sigma\right)$ , the  $\sigma$  MO contribution given by Eq. (14.630):

$$E_{T_{alkans}}(C-C) = 2(n-1)E_{T_{alkans}}(C-C,2sp^{3}) + E_{T_{alkans}}(C-C,\sigma)$$

$$= (n-1) \left\{ -\frac{e^{2}}{8\pi\varepsilon_{0}\sqrt{aa_{0}}} \left[ (0.91771)\left(2 - \frac{1}{2}\frac{a_{0}}{a}\right) \ln\frac{a + \sqrt{aa_{0}}}{a - \sqrt{aa_{0}}} - 1 \right] \right\}$$

$$= (n-1)\left(2(-0.92918 \ eV) + (-31.63537 \ eV)\right)$$

$$= -(n-1)33.49373 \ eV$$

$$(14.631)$$

#### VIBRATION OF CONTINUOUS-CHAIN ALKANES

The vibrational energy levels of the C-C bonds of  $C_nH_{2n+2}$  may be solved as n-1 sets of coupled carbon harmonic oscillators wherein each carbon is further coupled to two or three equivalent H harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

15

## THE DOPPLER ENERGY TERMS OF THE C-C-BOND MOs OF CONTINUOUS-CHAIN ALKANES

The equations of the radiation reaction force of each symmetrical C-C-bond MO are given by Eqs. (11.231-11.233), except the force-constant factor is 0.5 based on the force constant 20 k' of Eq. (14.152), and the C-C-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.5e^2}{4\pi\varepsilon_0 a^3}} = 9.43699 \ X \ 10^{15} \ rad/s \tag{14.632}$$

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where a is given by Eq. (14.523). The kinetic energy,  $E_K$ , is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar \omega = \hbar 9.43699 \, X \, 10^{15} \, rad \, / \, s = 6.21159 \, eV$$
 (14.633)

In Eq. (11.181), substitution of  $E_{T_{altans}}(C-C)$  (Eq. (14.631)) with n=2 for  $E_{h\nu}$ , the mass of the electron,  $m_e$ , for M, and the kinetic energy given by Eq. (14.633) for  $\overline{E}_K$  gives the Doppler energy of the electrons of each of the bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{Mc^2}} = -33.49373 \ eV \sqrt{\frac{2e(6.21159 \ eV)}{m_e c^2}} = -0.16515 \ eV$$
 (14.634)

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of each C-C-10 bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei,  $\overline{E}_{cse}$ , is given by the sum of the corresponding energies,  $\overline{E}_D$  given by Eq. (14.634) and  $\overline{E}_{Kvib}$ , the average kinetic energy of vibration which is 1/2 of the vibrational energy of each C-C bond. Using the ethane experimental C-C  $E_{vib}(v_3)$  of 993  $cm^{-1}$  (0.12312 eV) [10] for  $\overline{E}_{Kvib}$  of the transition state 15 having n-1 independent bonds,  $\overline{E}'_{alkane\ osc}(C-C,\sigma)$  per bond is

$$\overline{E}'_{alkane \ osc} \left( C - C, \sigma \right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}$$
(14.635)

$$\overline{E}'_{alkane\ osc}(C-C,\sigma) = -0.16515\ eV + \frac{1}{2}(0.12312\ eV) = -0.10359\ eV$$
 (14.636)

Given that the vibration and reentrant oscillation is for n-1 C-C bonds,  $\overline{E}_{alkane osc}(C-C,\sigma)$ , is:

$$\overline{E}_{alkane \ osc} (C - C, \sigma) = (n - 1) \left( \overline{E}_D + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$

$$= (n - 1) \left( -0.16515 \ eV + \frac{1}{2} (0.12312 \ eV) \right)$$

$$= -(n - 1) 0.10359 \ eV$$
(14.637)

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# TOTAL ENERGIES OF THE C-C-BOND MOs OF CONTINUOUS-CHAIN ALKANES

 $E_{alkaneT+osc}(C-C)$ , the total energy of the n-1 bonds of the C-C-bond MOs including the Doppler term, is given by the sum of  $E_{T_{alkane}}(C-C)$  (Eq. (14.631)) and  $\overline{E}_{alkane\ asc}(C-C,\sigma)$  5 given by Eq. (14.637):

$$E_{alkaneT+osc}\left(C-C\right) = \left(\left(n-1\right)\left(\begin{array}{c} V_e + T + V_m + V_p + E\left(C_{alkane}, 2sp^3\right) \\ + 2E_{T_{alkane}}\left(C-C, 2sp^3\right) \end{array}\right) + \overline{E}_{alkane\ osc}\left(C-C, \sigma\right) \right)$$

$$= E_{T_{alkane}}\left(C-C, \sigma\right) + 2\left(n-1\right)E_{T_{alkane}}\left(C-C, 2sp^3\right) + \overline{E}_{alkane\ osc}\left(C-C, \sigma\right)$$

$$= E_{T_{alkane}}\left(C-C\right) + \overline{E}_{alkane\ osc}\left(C-C, \sigma\right)$$

$$(14.638)$$

$$E_{alkaneT+osc}\left(C-C\right) = (n-1) \begin{cases} \left(\frac{-e^2}{8\pi\varepsilon_0 c'}\right) \left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \\ -15.56407 \ eV + 2E_{T_{alkane}}\left(C-C,2sp^3\right) \end{cases} \\ \left(\frac{2\hbar\sqrt{\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 a^3}}}{n_e}\right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \\ = (n-1)\left(-33.49373 \ eV - 0.16515 \ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{cases}$$
(14.639)

From Eqs. (14.637-14.639), the total energy of the n-1 bonds of the C-C-bond MOs is

$$E_{alkaneT+osc}(C-C) = (n-1)\left(-31.63537 \, eV + 2E_{T_{alkane}}\left(C-C, 2sp^{3}\right)\right) + \overline{E}_{alkane \, osc}\left(C-C, \sigma\right)$$

$$= (n-1)\left(-31.63537 \, eV + 2\left(-0.92918 \, eV\right)\right)$$

$$= -0.16515 \, eV + \frac{1}{2}(0.12312 \, eV)$$

$$= -(n-1)33.59732 \, eV$$
(14.640)

where the experimental  $E_{vib}$  was used for the  $\hbar \sqrt{\frac{k}{\mu}}$  term.

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# TOTAL BOND ENERGY OF THE C-C BONDS OF CONTINUOUS-CHAIN ALKANES

Since there are two carbon atoms per bond and the number of C-C bonds is n-1, the total bond energy of the C-C bonds of  $C_nH_{2n+2}$ ,  $E_D(C-C)_{n-1}$ , is given by  $2(n-1)E(C,2sp^3)$ 

5 minus  $E_{alkaneT+osc}(C-C)$  (Eq. (14.640)) where  $E(C,2sp^3)$  (Eq. (14.146)) is the initial energy of each  $C2sp^3$  HO of the  $CH_3$  and  $CH_2$  groups that bond to the C-C bonds. Thus, the total dissociation energy of the C-C bonds of  $C_nH_{2n+2}$ , is

$$E_{D}(C-C)_{n-1} = 2(n-1)(E(C,2sp^{3})) - (E_{alakneT+asc}(C-C))$$

$$= 2(n-1)(-14.63489 eV) - (n-1)(-33.59732 eV)$$

$$= (n-1)(2(-14.63489 eV) - (-33.59732 eV))$$

$$= (n-1)(4.32754 eV)$$
(14.641)

## 10 TOTAL ENERGY OF CONTINUOUS-CHAIN ALKANES

 $E_D(C_nH_{2n+2})$ , the total bond dissociation energy of  $C_nH_{2n+2}$ , is given as the sum of the energy components due to the two methyl groups, n-2 methylene groups, and n-1 C-C bonds where each energy component is given by Eqs. (14.590), (14.625), and (14.641), respectively. Thus, the total bond dissociation energy of  $C_nH_{2n+2}$  is

$$E_{D}(C_{n}H_{2n+2}) = E_{D}(C-C)_{n-1} + 2E_{D_{alkane}}(^{12}CH_{3}) + (n-2)E_{D_{alkane}}(^{12}CH_{2})$$

$$= (n-1)(4.32754 \text{ eV}) + 2(12.49186 \text{ eV}) + (n-2)(7.83016 \text{ eV})$$
(14.642)

The experimental total bond dissociation energy of  $C_nH_{2n+2}$ ,  $E_{D_{exp}}\left(C_nH_{2n+2}\right)$ , is given by the negative difference between the enthalpy of its formation  $(\Delta H_f\left(C_nH_{2n+2}\left(gas\right)\right))$  and the sum of the enthalpy of the formation of the reactant gaseous carbons  $(\Delta H_f\left(C\left(gas\right)\right))$  and hydrogen  $(\Delta H_f\left(H\left(gas\right)\right))$  atoms:

$$E_{D_{\exp}}(C_n H_{2n+2}) = -\left\{ \Delta H_f(C_n H_{2n+2}(gas)) - \left[ n\Delta H_f(C(gas)) + (2n+2)\Delta H_f(H(gas)) \right] \right\}$$

$$= -\left\{ \Delta H_f(C_n H_{2n+2}(gas)) - \left[ n7.42774 \ eV + (2n+2)2.259353 \ eV \right] \right\}$$
(14.643)

where the heats of formation atomic carbon and hydrogen gas are given by [17-18]

$$\Delta H_{I}(C(gas)) = 716.68 \, kJ \, / \, mole \, (7.42774 \, eV \, / \, molecule)$$
 (14.644)

$$\Delta H_f(H(gas)) = 217.998 \ kJ / mole (2.259353 \ eV / molecule)$$
 (14.645)

Using the corresponding experimental  $\Delta H_f\left(C_nH_{2n+2}\left(gas\right)\right)$  [18],  $E_D\left(C_nH_{2n+2}\right)$  was determined from propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane in the corresponding sections, and the results of the determination of the total energies are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Using the results for  $C_nH_{2n+2}$  and the functional groups as basis sets that are linearly combined, the exact solution for the dimensional parameters, charge density functions, and energies of all molecules can be obtained. For example, one or more of the hydrogen atoms of the solution for  $C_nH_{2n+2}$  can be substituted with one or more of the previously solved functional groups or derivative functional groups to give a desired molecule. The solution is given by energy matching each group to  $C_nH_{2n+2}$ . Substitution of one or more H's of  $C_nH_{2n+2}$  with functional groups from the list of  $CH_3$ , other  $C_nH_{2n+2}$  groups,  $H_2C = CH_2$ ,  $HC \equiv CH$ , F, Cl, O, OH, NH,  $NH_2$ , CN, NO,  $NO_2$ , CO,  $CO_2$ , and  $C_6H_6$  give the solutions of branched alkanes, alkenes, and alkynes, alkyl halides, ethers, alcohols, amides, amines, nitriles, alkyl nitrosos, alkyl nitrates, aldehydes, ketones, carbolylic acids, esters, and substituted aromatics.

### PROPANE $(C_3H_8)$

20 Using Eq. (14.642) with n=3, the total bond dissociation energy of  $C_3H_8$  is

$$E_D(C_3H_8) = E_D(C-C)_2 + 2E_{D_{effront}} (^{12}CH_3) + E_{D_{oblase}} (^{12}CH_2)$$

$$= (2)(4.32754 \, eV) + (2)(12.49186 \, eV) + (1)(7.83016 \, eV)$$

$$= 41.46896 \, eV$$
(14.646)

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_3H_8$ ,  $E_{D_{exp}}(C_3H_8)$ , given by the negative difference between the enthalpy of its formation  $(\Delta H_f(C_3H_8(gas)=-1.0758\ eV))$  [18] and the sum of the enthalpy of the formation of the

25 gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen  $(\Delta H_f(H(gas)))$  atoms is

$$E_{D_{exp}}(C_3H_8) = -\left\{\Delta H_f(C_3H_8(gas)) - \left[3\Delta H_f(C(gas)) + 8\Delta H_f(H(gas))\right]\right\}$$

$$= -\left\{-1.0758 \ eV - \left[(3)7.42774 \ eV + (8)2.259353 \ eV\right]\right\}$$

$$= 41.434 \ eV$$
(14.647)

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The charge-density of the  $C_3H_8$  molecular orbital (MO) comprising a linear combination of two methyl groups and one methylene group is shown in Figure 50.

#### BUTANE $(C_{A}H_{10})$

5 Using Eq. (14.642) with n=4, the total bond dissociation energy of  $C_4H_{10}$  is

10 gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms is

$$E_D(C_4H_{10}) = E_D(C-C)_3 + 2E_{D_{alkows}} (^{12}CH_3) + 2E_{D_{alkows}} (^{12}CH_2)$$

$$= (3)(4.32754 \, eV) + (2)(12.49186 \, eV) + (2)(7.83016 \, eV)$$

$$= 53.62666 \, eV$$
(14.648)

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_4H_{10}$ ,  $E_{D_{exp}}(C_4H_{10})$ , given by the negative difference between the enthalpy of its formation  $(\Delta H_f(C_4H_{10}(gas)=-1.3028\ eV))$  [18] and the sum of the enthalpy of the formation of the

$$E_{D_{exp}}(C_4H_{10}) = -\left\{\Delta H_f(C_4H_{10}(gas)) - \left[4\Delta H_f(C(gas)) + 10\Delta H_f(H(gas))\right]\right\}$$

$$= -\left\{-1.3028 \ eV - \left[(4)7.42774 \ eV + (10)2.259353 \ eV\right]\right\}$$

$$= 53.61 \ eV$$
(14.649)

The charge-density of the  $C_4H_{10}$  molecular orbital (MO) comprising a linear combination of two methyl and two methylene groups is shown in Figure 51.

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#### **PENTANE** $(C_5H_{12})$ .

Using Eq. (14.642) with n=5, the total bond dissociation energy of  $C_5H_{12}$  is

$$E_{D}(C_{5}H_{12}) = E_{D}(C-C)_{4} + 2E_{D_{altorice}} (^{12}CH_{3}) + 3E_{D_{altorice}} (^{12}CH_{2})$$

$$= (4)(4.32754 \, eV) + (2)(12.49186 \, eV) + (3)(7.83016 \, eV)$$

$$= 65.78436 \, eV$$
(14.650)

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_5H_{12}$ ,  $E_{D_{exp}}(C_5H_{12})$ , 20 given by the negative difference between the enthalpy of its formation  $(\Delta H_f(C_5H_{12}(gas)=-1.5225\ eV))$  [18] and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen  $(\Delta H_f(H(gas)))$  atoms is

$$437$$

$$E_{D_{\text{cap}}}(C_5 H_{12}) = -\left\{ \Delta H_f \left( C_5 H_{12} \left( gas \right) \right) - \left[ 5 \Delta H_f \left( C \left( gas \right) \right) + 12 \Delta H_f \left( H \left( gas \right) \right) \right] \right\}$$

$$= -\left\{ -1.5225 \ eV - \left[ (5)7.42774 \ eV + (12)2.259353 \ eV \right] \right\}$$

$$= 65.77 \ eV$$

$$(14.651)$$

The charge-density of the  $C_5H_{12}$  molecular orbital (MO) comprising a linear combination of two methyl and three methylene groups is shown in Figure 52.

#### 5 HEXANE $(C_6H_{14})$

Using Eq. (14.642) with n=6, the total bond dissociation energy of  $C_6H_{14}$  is

$$E_D(C_6H_{14}) = E_D(C-C)_5 + 2E_{D_{ellume}} (^{12}CH_3) + 4E_{D_{ellume}} (^{12}CH_2)$$

$$= (5)(4.32754 \, eV) + (2)(12.49186 \, eV) + (4)(7.83016 \, eV)$$

$$= 77.94206 \, eV$$
(14.652)

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_6H_{14}$ ,  $E_{D_{exp}}\left(C_6H_{14}\right)$ , given by the negative difference between the enthalpy of its formation  $(\Delta H_f\left(C_6H_{14}\left(gas\right)=-1.7298\ eV\right))$  [18] and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f\left(C\left(gas\right)\right))$  and hydrogen  $(\Delta H_f\left(H\left(gas\right)\right))$  atoms is

$$E_{D_{exp}}(C_6H_{14}) = -\left\{\Delta H_f(C_6H_{14}(gas)) - \left[6\Delta H_f(C(gas)) + 14\Delta H_f(H(gas))\right]\right\}$$

$$= -\left\{-1.7298 \ eV - \left[(6)7.42774 \ eV + (14)2.259353 \ eV\right]\right\}$$

$$= 77.93 \ eV$$
(14.653)

The charge-density of the  $C_6H_{14}$  molecular orbital (MO) comprising a linear combination of two methyl and four methylene groups is shown in Figure 53.

#### **HEPTANE** $(C_7H_{16})$

Using Eq. (14.642) with n=7, the total bond dissociation energy of  $C_7H_{16}$  is

$$E_D(C_7 H_{16}) = E_D(C - C)_6 + 2E_{D_{allows}} (^{12}CH_3) + 5E_{D_{allows}} (^{12}CH_2)$$

$$= (6)(4.32754 \, eV) + (2)(12.49186 \, eV) + (5)(7.83016 \, eV)$$

$$= 90.09976 \, eV$$
(14.654)

20 Using Eq. (14.643), the experimental total bond dissociation energy of  $C_7H_{16}$ ,  $E_{D_{exp}}(C_7H_{16})$ , given by the negative difference between the enthalpy of its formation

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 $(\Delta H_f(C_7H_{16}(gas) = -1.9443 \ eV))$  [18] and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen  $(\Delta H_f(H(gas)))$  atoms is

$$\begin{split} E_{D_{\text{cop}}}\left(C_{7}H_{16}\right) &= -\left\{\Delta H_{f}\left(C_{7}H_{16}\left(gas\right)\right) - \left[7\Delta H_{f}\left(C\left(gas\right)\right) + 16\Delta H_{f}\left(H\left(gas\right)\right)\right]\right\} \\ &= -\left\{-1.9443\ eV - \left[\left(7\right)7.42774\ eV + \left(16\right)2.259353\ eV\right]\right\} \\ &= 90.09\ eV \end{split}$$

5 The charge-density of the  $C_7H_{16}$  MO comprising a linear combination of two methyl and five methylene groups is shown in Figure 54.

#### OCTANE $(C_8H_{18})$

(14.655)

Using Eq. (14.642) with n = 8, the total bond dissociation energy of  $C_8H_{18}$  is

$$E_D(C_8H_{18}) = E_D(C - C)_7 + 2E_{D_{alkare}} {12CH_3} + 6E_{D_{alkare}} {12CH_2}$$

$$= (7)(4.32754 \ eV) + (2)(12.49186 \ eV) + (6)(7.83016 \ eV)$$

$$= 102.25746 \ eV$$
(14.656)

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_8H_{18}$ ,  $E_{D_{exp}}(C_8H_{18})$ , given by the negative difference between the enthalpy of its formation  $(\Delta H_f(C_8H_{18}(gas) = -2.1609 \, eV))$  [18] and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen  $(\Delta H_f(H(gas)))$  atoms is

$$E_{D_{exp}}(C_8H_{18}) = -\left\{\Delta H_f(C_8H_{18}(gas)) - \left[8\Delta H_f(C(gas)) + 18\Delta H_f(H(gas))\right]\right\}$$

$$= -\left\{-2.1609 \ eV - \left[(8)7.42774 \ eV + (18)2.259353 \ eV\right]\right\}$$

$$= 102.25 \ eV$$

$$(14.657)$$

The charge-density of the  $C_8H_{18}$  MO comprising a linear combination of two methyl and six methylene groups is shown in Figure 55.

## 20 NONANE $(C_9H_{20})$

Using Eq. (14.642) with n=9, the total bond dissociation energy of  $C_9H_{20}$  is

$$E_{D}(C_{9}H_{20}) = E_{D}(C - C)_{8} + 2E_{D_{olkansr}} (^{12}CH_{3}) + 7E_{D_{olkansr}} (^{12}CH_{2})$$

$$= (8)(4.32754 \, eV) + (2)(12.49186 \, eV) + (7)(7.83016 \, eV)$$

$$= 114.41516 \, eV$$
(14.658)

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_9H_{20}$ ,  $E_{D_{exp}}(C_9H_{20})$ , given by the negative difference between the enthalpy of its formation  $(\Delta H_f(C_9H_{20}(gas)=-2.3651\ eV))$  [18] and the sum of the enthalpy of the formation of the

5 gaseous carbons ( $\Delta H_f(C(gas))$ ) and hydrogen ( $\Delta H_f(H(gas))$ ) atoms is

$$E_{D_{cop}}(C_9H_{20}) = -\left\{\Delta H_f(C_9H_{20}(gas)) - \left[9\Delta H_f(C(gas)) + 20\Delta H_f(H(gas))\right]\right\}$$

$$= -\left\{-2.3651 \ eV - \left[(9)7.42774 \ eV + (20)2.259353 \ eV\right]\right\}$$

$$= 114.40 \ eV$$

$$(14.659)$$

The charge-density of the  $C_9H_{20}$  MO comprising a linear combination of two methyl and seven methylene groups is shown in Figure 56.

10

#### **DECANE** $(C_{10}H_{22})$

Using Eq. (14.642) with n=10, the total bond dissociation energy of  $C_{10}H_{22}$  is

$$E_D(C_{10}H_{22}) = E_D(C - C)_9 + 2E_{D_{allums}} (^{12}CH_3) + 8E_{D_{allums}} (^{12}CH_2)$$

$$= (9)(4.32754 \, eV) + (2)(12.49186 \, eV) + (8)(7.83016 \, eV)$$

$$= 126.57286 \, eV$$
(14.660)

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_{10}H_{22}$ , 15  $E_{D_{exp}}(C_{10}H_{22})$ , given by the negative difference between the enthalpy of its formation  $(\Delta H_f(C_{10}H_{22}(gas) = -2.5858 \, eV))$  [18] and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen  $(\Delta H_f(H(gas)))$  atoms is

$$E_{D_{exp}}(C_{10}H_{22}) = -\left\{\Delta H_f\left(C_{10}H_{22}(gas)\right) - \left[10\Delta H_f\left(C(gas)\right) + 22\Delta H_f\left(H(gas)\right)\right]\right\}$$

$$= -\left\{-2.5858 \ eV - \left[\left(10\right)7.42774 \ eV + \left(22\right)2.259353 \ eV\right]\right\}$$

$$= 126.57 \ eV$$
(14.661)

20 The charge-density of the  $C_{10}H_{22}$  molecular orbital (MO) comprising a linear combination of two methyl and eight methylene groups is shown in Figure 57.

### UNDECANE $(C_{11}H_{24})$

Using Eq. (14.642) with n = 11, the total bond dissociation energy of  $C_{11}H_{24}$  is

$$E_D(C_{11}H_{24}) = E_D(C - C)_{10} + 2E_{D_{albane}}(^{12}CH_3) + 9E_{D_{albane}}(^{12}CH_2)$$

$$= (10)(4.32754 \ eV) + (2)(12.49186 \ eV) + (9)(7.83016 \ eV)$$

$$= 138.73056 \ eV$$
(14.662)

5 Using Eq. (14.643), the experimental total bond dissociation energy of  $C_{11}H_{24}$ ,  $E_{D_{exp}}(C_{11}H_{24})$ , given by the negative difference between the enthalpy of its formation  $(\Delta H_f(C_{11}H_{24}(gas) = -2.8066 \, eV))$  [18] and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen  $(\Delta H_f(H(gas)))$  atoms is

$$E_{D_{cap}}(C_{11}H_{24}) = -\left\{\Delta H_f(C_{11}H_{24}(gas)) - \left[11\Delta H_f(C(gas)) + 24\Delta H_f(H(gas))\right]\right\}$$

$$= -\left\{-2.8066 \ eV - \left[(11)7.42774 \ eV + (24)2.259353 \ eV\right]\right\}$$

$$= 138.736 \ eV$$

10 (14.663)

The charge-density of the  $C_{11}H_{24}$  MO comprising a linear combination of two methyl and nine methylene groups is shown in Figure 58.

## 15 **DODECANE** $(C_{12}H_{26})$

Using Eq. (14.642) with n=12, the total bond dissociation energy of  $C_{12}H_{26}$  is

$$E_D(C_{12}H_{26}) = E_D(C - C)_{11} + 2E_{D_{alkansr}}(^{12}CH_3) + 10E_{D_{alkansr}}(^{12}CH_2)$$

$$= (11)(4.32754 \, eV) + (2)(12.49186 \, eV) + (10)(7.83016 \, eV) \qquad (14.664)$$

$$= 150.88826 \, eV$$

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_{12}H_{26}$ ,  $E_{D_{exp}}(C_{12}H_{26})$ , given by the negative difference between the enthalpy of its formation 20  $(\Delta H_f(C_{12}H_{26}(gas) = -2.9994 \, eV))$  [18] and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen  $(\Delta H_f(H(gas)))$  atoms is

$$E_{D_{cop}}(C_{12}H_{26}) = -\left\{\Delta H_f(C_{12}H_{26}(gas)) - \left[12\Delta H_f(C(gas)) + 26\Delta H_f(H(gas))\right]\right\}$$

$$= -\left\{-2.9994 \ eV - \left[(12)7.42774 \ eV + (26)2.259353 \ eV\right]\right\}$$

$$= 150.88 \ eV$$
(14.665)

The charge-density of the  $C_{12}H_{26}$  MO comprising a linear combination of two methyl and ten methylene groups is shown in Figure 59.

#### 5 OCTADECANE $(C_{18}H_{38})$

Using Eq. (14.642) with n=18, the total bond dissociation energy of  $C_{18}H_{38}$  is

$$E_{D}(C_{18}H_{38}) = E_{D}(C - C)_{17} + 2E_{D_{alborne}}(^{12}CH_{3}) + 16E_{D_{alborne}}(^{12}CH_{2})$$

$$= (17)(4.32754 \ eV) + (2)(12.49186 \ eV) + (16)(7.83016 \ eV)$$

$$= 223.83446 \ eV$$
(14.666)

Using Eq. (14.643), the experimental total bond dissociation energy of  $C_{18}H_{38}$ ,  $E_{D_{exp}}(C_{18}H_{38})$ , given by the negative difference between the enthalpy of its formation  $(\Delta H_f(C_{18}H_{38}(gas) = -4.2970 \ eV))$  [18] and the sum of the enthalpy of the formation of the gaseous carbons  $(\Delta H_f(C(gas)))$  and hydrogen  $(\Delta H_f(H(gas)))$  atoms is

$$\begin{split} E_{D_{cop}}\left(C_{18}H_{38}\right) &= -\left\{\Delta H_f\left(C_{18}H_{38}\left(gas\right)\right) - \left[18\Delta H_f\left(C\left(gas\right)\right) + 38\Delta H_f\left(H\left(gas\right)\right)\right]\right\} \\ &= -\left\{-4.2970\ eV - \left[\left(18\right)7.42774\ eV + \left(38\right)2.259353\ eV\right]\right\} \\ &= 223.85\ eV \end{split}$$

(14.667)

The charge-density of the  $C_{18}H_{38}$  molecular orbital (MO) comprising a linear combination of two methyl and sixteen methylene groups is shown in Figure 60.

Table 14.1. The calculated and experimental bond parameters of  $CO_2$ ,  $NO_2$ ,  $CH_3CH_3$ ,  $CH_2CH_2$ , CHCH, benzene, propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane.

Parameter	Calculated	Experimental	Ref. for Exp.
CO <sub>2</sub> Bond Energy	5.49553 eV	5.51577 eV	7
$CO_2$ Bond Length	1.1616 Å	1.1600 Å	3

11	2
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Parameter	Calculated	Experimental	Ref. for Exp.			
NO <sub>2</sub> Bond Energy	3.1532 eV	3.161 eV	7			
NO <sub>2</sub> Bond Length	1.1872 Å	1.193 Å	3			
$NO_2$ Bond Angle	131.012°	134.1°	3			
$H_3C-CH_3$ Bond Energy	3.90245 eV	3.8969 eV	. 7			
$H_3C-CH_3$ Bond Length	1.53635 Å	1.5351 Å	3			
$H-CH_2CH_3$ Bond Length	1.10822 Å	1.0940 Å	3			
Ethane $H-C-H$ Bond Angle	107.44°	107.4°	8			
Ethane $C-C-H$ Bond Angle	111.44°	111.17°	3			
$H_2C = CH_2$ Bond Energy	7.55681 eV	7.597 eV	7			
$H_2C = CH_2$ Bond Length	1.3405 Å	1.339 Å	3			
$H-CHCH_2$ Bond Length	1.0826 Å	1.087 Å	3			
Ethylene $H-C-H$ Bond Angle	116.31°	116.6°	11			
Ethylene $C = C - H$ Bond Angle	121.85°	121.7°	11			
$HC \equiv CH$ Bond Energy	10.07212 eV	10.0014 eV	7			
$HC \equiv CH$ Bond Length	1.2007 Å	1.203 Å	3			
H-CCH Bond Length	1.0538 Å	1.060 Å	3			
Acetylene $C \equiv C - H$ Bond Angle	180°	180°	6			
$C_6H_6$ Total Bond Energy	57.2601 eV	57.26 eV	17-18			
Benzene $C = C$ Bond Length	1.3914 Å	1.399 Å	3			
$H - C_6 H_5$ Bond Length	1.0933 Å	1.101 Å	3			
$C_6H_6$ $C=C=C$ Bond Angle	120°	120°	13-15			
$C_6H_6$ $C=C-H$ Bond Angle	12 <b>0°</b>	120°	13-15			
$C_3H_8$ Total Bond Energy	41.46896 eV	41.434 eV	17-18			
Propane $C-C$ Bond Length	1.5428 Å	1.532 Å	3			
Propane $C-H$ Bond Length	1. <b>1097 Å</b>	1.1 <b>07</b> Å	3			
Alkane $H-C-H$ Bond Angle	109.50°	109.3°	19			
Alkane $C-C-H$ Bond Angle	109.44°	109.3°	19			
$C_4H_{10}$ Total Bond Energy	53.62666 eV	53.61 eV	17-18			
Butane $C-C$ Bond Length	1.5428 Å	1.531 Å	3			
Butane $C-H$ Bond Length	1.11713 Å	1.117 Å	3			

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Parameter	Calculated	Experimental	Ref. for Exp.
$C_5H_{12}$ Total Bond Energy	65.78436 eV	65.77 eV	17-18
$C_6H_{14}$ Total Bond Energy	77.94206 eV	77.93 eV	17-18
$C_7H_{16}$ Total Bond Energy	90.09976 eV	90.09 eV	17-18
$C_8H_{18}$ Total Bond Energy	102.25746 eV	102.25 eV	17-18
$C_9H_{20}$ Total Bond Energy	114.41516 eV	114.40 eV	17-18
$C_{\rm 10}H_{\rm 22}$ Total Bond Energy	126.57286 eV	126.57 eV	17-18
$C_{11}H_{24}$ Total Bond Energy	138.73056 eV	138.736 eV	17-18
$C_{12}H_{26}$ Total Bond Energy	150.88826 eV	150.88 eV	17-18
C <sub>18</sub> H <sub>38</sub> Total Bond Energy	223.83446 eV	223.85 eV	17-18

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#### I CLAIM:

A system of computing and rendering the nature of at least one specie selected from a
group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic
molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any
functional group therein, comprising physical, Maxwellian solutions of charge, mass, and
current density functions of said specie, said system comprising:

processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and

- an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.
  - 2. The system of claim 1 wherein the output device is a display that displays at least one of visual or graphical media.

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- 3. The system of claim 2 wherein the display is at least one of static or dynamic.
- 4. The system of claim 3 wherein at least one of vibration and rotation is be displayed.
- 20 5. The system of claim 4 wherein displayed information is used to model reactivity and physical properties.
  - 6. The system of claim 5, wherein the output device is a monitor, video projector, printer, or three-dimensional rendering device.

25

- 7. The system of claim 6 wherein displayed information is used to model other species and provides utility to anticipate their reactivity and physical properties.
- 8. The system of claim 7 wherein the processing means is a general purpose computer.

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9. The system of claim 8 wherein the general purpose computer comprises a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input means.

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- 10. The system of claim 9, wherein the input means comprises a serial port, usb port, microphone input, camera input, keyboard or mouse.
- 5 11. The system of claim 10 wherein the processing means comprises a special purpose computer or other hardware system.
  - 12. The system of claim 11 further comprising computer program products.
- 10 13. The system of claim 12 further comprising computer readable medium having embodied therein program code means.
  - 14. The system of claim 13 wherein the computer readable media is any available media which can be accessed by a general purpose or special purpose computer.
- 15. The system of claim 14 wherein the computer readable media comprises at least one of RAM, ROM, EPROM, CD ROM, DVD or other optical disk storage, magnetic disk storage or other magnetic storage devices, or any other medium which can embody the desired program code means and which can be accessed by a general purpose or special purpose 20 computer.
  - 16. The system of claim 15 wherein the program code means comprises executable instructions and data which cause a general purpose computer or special purpose computer to perform a certain function of a group of functions.
  - 17. The system of claim 16 wherein the program code is Mathematica programmed with an algorithm based on the physical solutions, and the computer is a PC.
- 18. The system of claim 17 wherein the algorithm is ParametricPlot3D[{2\*Sqrt[1-30 z\*z]\*Cos[u],Sqrt[(1-z\*z)]\*Sin[u],z},{u,0,2\* Pi},{z,-1,.9999}], and the rendering is viewed from different perspectives.

- 19. The system of claim 18 wherein the algorithms for viewing from different perspectives comprises Show[Out[1], ViewPoint->{x,y,z}] where x, y, and z are Cartesian coordinates.
- 20. The system of claim 19 wherein the physical, Maxwellian solutions of the charge, mass, and current density functions of said specie comprises a solution of the classical wave equation  $\left[\nabla^2 \frac{1}{v^2} \frac{\partial^2}{\partial t^2}\right] \rho(r, \theta, \phi, t) = 0$  which is the equation of motion of the charge.
  - 21. The system of claim 20 wherein the boundary constraint of the wave equation solution is nonradiation according to Maxwell's equations.
- 22. The system of claim 21 wherein the boundary condition is met for an ellipsoidal-time harmonic function when

$$\omega_n = \frac{\pi\hbar}{m_e A} = \frac{\hbar}{m_e ab}$$

where the area of an ellipse is

15 
$$A = \pi ab$$

10

where 2b is the length of the semiminor axis and 2a is the length of the semimajor axis.

23. The system of claim 22 wherein the specie charge and current density functions, bond distance, and energies are solved from the Laplacian in ellipsoidal coordinates:

$$(\eta - \zeta)R_{\xi}\frac{\partial}{\partial \xi}(R_{\xi}\frac{\partial \phi}{\partial \xi}) + (\zeta - \xi)R_{\eta}\frac{\partial}{\partial \eta}(R_{\eta}\frac{\partial \phi}{\partial \eta}) + (\xi - \eta)R_{\zeta}\frac{\partial}{\partial \zeta}(R_{\zeta}\frac{\partial \phi}{\partial \zeta}) = 0.$$

with the constraint of nonradiation.

24. The system of claim 23 wherein each bond of the said specie defined as a molecular orbital (MO) has the ellipsoidal charge-density function given by

25 
$$\sigma = \frac{q}{4\pi abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$

25. The system of claim 24 wherein the bonds of the said specie defined as a molecular orbital (MO) has the charge-density function comprising a linear combination of ellipsoids wherein the charge density of one said ellipsoid is given by

$$\sigma = \frac{q}{4\pi abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$

26. The system of claim 25 wherein the equation of motion has the parametric form  $r(t) = \mathbf{i}a \cos \omega t + \mathbf{j}b \sin \omega t$ 

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27. The system of claim 26 wherein he force balance of the hydrogen-type molecular ion ellipsoidal MO is given by

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{p e^2}{8\pi \varepsilon_0} D$$

$$a=2a_0$$

10

28. The system of claim 27 where the force constant k of a  $H_2^+$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k = \frac{2e^2}{4\pi\varepsilon_0}$$

15 29. The system of claim 28 wherein the distance from the origin of the  $H_2$ -type-ellipsoidal-MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}}$$

30. The system of claim 29 wherein the internuclear distance 2c' is given by:

$$2c' = 2\sqrt{\frac{aa_0}{2}}$$

31. The system of claim 30 wherein the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO b=c is given by:

$$b = \sqrt{a^2 - c'^2}$$

25

32. The system of claim 31 wherein the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO b=c is given by:

$$e = \frac{c'}{a}$$

5 33. The system of claim 32 wherein the internuclear distance, 2c', which is the distance between the foci is

$$2c'=2a_o;$$

the semiminor axis is

$$b = \sqrt{3}a_0$$
, and

10 the eccentricity, e, is

15

$$e=\frac{1}{2}.$$

34. The system of claim 33 wherein the potential energy of the electron in the central field of the protons at the foci is

$$V_{e} = \frac{-4e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}}$$

$$= \frac{-4e^{2}}{8\pi\varepsilon_{o}c'} \ln \frac{a + c'}{a - c'}$$

$$= \frac{-4e^{2}}{8\pi\varepsilon_{o}a_{H}} \ln 3 = -59.7575 \ eV$$

The potential energy of the two protons is

$$V_p = \frac{e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} = \frac{e^2}{8\pi\varepsilon_o a_H} = 13.5984 \ eV;$$

The kinetic energy of the electron is

$$T = \frac{2\hbar^2}{m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = \frac{2e^2}{8\pi\varepsilon_o a_H} \ln 3 = 29.8787 \ eV \text{ , and}$$

20 The total energy,  $E_T$ , is given by the sum of the energy terms:

$$E_T = V_e + T + V_p$$

$$E_{T} = \frac{-e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}} \left[ \left( 4 - \frac{4}{a} \right) \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right]$$

$$= \frac{-e^{2}}{8\pi\epsilon_{o}a_{H}} (4 \ln 3 - 1 - 2 \ln 3)$$

$$= -16.2803 \ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

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35. The system of claim 34 wherein during bond formation, the electron undergoes a reentrant oscillatory orbit with vibration of the protons, and the corresponding energy  $\overline{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{asc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_p\right) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
, and

10 The total energy is

$$E_T = V_e + T + V_p + \overline{E}_{osc}$$

$$E_{T} = -\left\{ \frac{e^{2}}{8\pi\varepsilon_{o}a_{H}} (4\ln 3 - 1 - 2\ln 3) \left[ 1 + \sqrt{\frac{2e^{2}}{4\pi\varepsilon_{o}(2a_{H})^{3}}} \frac{1}{m_{e}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\}$$

$$= -16.2803 \ eV - 0.118811 \ eV + \frac{1}{2} (0.29282 \ eV)$$

$$= -16.2527 \ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

15

36. The system of claim 35 wherein the bond dissociation energy,  $E_D$ , is the difference between the total energy of the hydrogen atom and  $E_T$ :

$$E_D = E(H) - E_T = 2.654 \ eV$$

20 wherein the total energy of a hydrogen atom is

 $E(H) = -13.59844 \, eV$ , wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm 10\%$ , if desired.

37. The system of claim 36 wherein the  $H_2^+$ -type ellipsoidal MO and the hydrogen atomic orbital (AO) serve as basis functions for the MOs of specie.

5

- 38. The system of claim 37 wherein the MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy,
- 10 (3) be stable to radiation, and (4) conserve the electron angular momentum of  $\hbar$ .
  - 39. The system of claim 38 wherein the potential energy of electron in the central field of the protons at the foci is

$$V_{e} = \frac{-4e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} = \frac{-4e^{2}}{8\pi\varepsilon_{o}c'} \ln \frac{a + c'}{a - c'};$$

15 The potential energy of the two protons is

$$V_p = \frac{e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} = \frac{e^2}{8\pi\varepsilon_o c'};$$

The kinetic energy of the electron is

$$T = \frac{2\hbar^2}{m_a a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = \frac{2\hbar^2}{m_e a c'} \ln \frac{a + c'}{a - c'}, \text{ and}$$

The total energy,  $E_{r}$ , is given by the sum of the energy terms:

 $E_T = V_e + T + V_p$ 

$$E_{T} = \frac{-e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}} \left[ \left( 4 - \frac{4}{a} \right) \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right] = \frac{-e^{2}}{8\pi\varepsilon_{o}c'} \left[ \left( 4 - \frac{4}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right].$$

- 40. The system of claim 39 wherein during bond formation, the electron undergoes a reentrant oscillatory orbit with vibration of the protons, and the corresponding energy  $\overline{E}_{osc}$  is
- 25 the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_p\right) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
, and

The total energy is

$$E_T = V_e + T + V_p + \overline{E}_{osc}$$

$$E_{T} = -\left\{ \frac{-e^{2}}{8\pi\varepsilon_{o}c'} \left[ \left( 4 - \frac{4}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \left[ 1 + \sqrt{\frac{\frac{2e^{2}}{4\pi\varepsilon_{o}(a)^{3}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right\}$$

5 41. The system of claim 40 wherein the force balance equation derived of a  $H_2$ -type ellipsoidal MO is given by

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{pe^2}{8\pi \varepsilon_o a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D$$

$$a = \frac{a_0}{2}$$

42. The system of claim 41 where the force constant k of a  $H_2$ -type ellipsoidal MO due to 10 the equivalent of two point charges of at the foci is given by:

$$k = \frac{2e^2}{4\pi\varepsilon_0}$$

43. The system of claim 42 wherein the distance from the origin of the  $H_2$ -type-ellipsoidal-MO to each focus c' is given by :

15 
$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}}$$

44. The system of claim 43 wherein the internuclear distance 2c' is given by:

$$2c' = 2\sqrt{\frac{aa_0}{2}}$$

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45. The system of claim 44 wherein the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO b=c is given by:

$$b = \sqrt{a^2 - c'^2}$$

46. The system of claim 45 wherein the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO b=c is given by:

$$e = \frac{c'}{a}$$

5

47. The system of claim 46 wherein the internuclear distance, 2c', which is the distance between the foci is

$$2c' = \sqrt{2}a_o;$$

the semiminor axis is

$$b = \frac{1}{\sqrt{2}} a_o, \text{ and }$$

the eccentricity, e, is

$$e = \frac{1}{\sqrt{2}}$$

48. The system of claim 47 wherein the potential energy of the two electrons in the central field of the protons at the foci is

$$V_e = \frac{-2e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -67.8358 \ eV ;$$

The potential energy of the two protons is

$$V_p = \frac{e^2}{8\pi\varepsilon_a\sqrt{a^2 - b^2}} = 19.2415 \ eV$$
;

The kinetic energy of the electrons is

20 
$$T = \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = 33.9179 \text{ eV}, \text{ and}$$

The energy,  $V_m$ , of the magnetic force between the electrons is

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} = -16.9589 \text{ eV}$$
, and

The total energy,  $E_T$ , is given by the sum of the energy terms:

$$E_T = V_e + T + V_m + V_p$$

$$E_T = -13.60 \ eV \left[ \left( 2p^2 \sqrt{2} - p^2 \sqrt{2} + \frac{p^2 \sqrt{2}}{2} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - p^2 \sqrt{2} \right] = -p^2 31.63$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

5 49. The system of claim 48 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the protons, and the corresponding energy  $\overline{E}_{asc}$  is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$\begin{split} E_T &= - \left\{ \frac{e^2}{8\pi\varepsilon_o a_0} \left[ \left( 2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2} + 1}{\sqrt{2} - 1} - \sqrt{2} \right] \left[ 1 + \sqrt{\frac{e^2}{4\pi\varepsilon_o a_0^3}} \frac{1}{m_e} \right] - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right] \\ &= -31.635 \ eV - 0.326469 \ eV + \frac{1}{2} \left( 0.56764 \ eV \right) \\ &= -31.6776 \ eV \end{split}$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm 10\%$ , if desired.

15 50. The system of claim 49 wherein the bond dissociation energy,  $E_D$ , is the difference between the total energy of the hydrogen atoms and  $E_T$ :

$$E_D = E(2H[a_H]) - E_T = 4.478 \ eV$$

wherein the total energy of two hydrogen atoms is

 $E(2H[a_H]) = -27.21 \, eV$ , wherein the calculated and measured values and constants recited 20 in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

51. The system of claim 50 wherein the  $H_2$ -type ellipsoidal MO and the hydrogen atomic orbital (AO) serve as basis functions for the MOs of the specie.

52. The system of claim 51 wherein the MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of  $\hbar$ .

5

53. The system of claim 52 wherein the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = \frac{-2e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}};$$

The potential energy of the two nuclei is

$$V_{p} = \frac{e^2}{8\pi\varepsilon_{o}\sqrt{a^2 - b^2}};$$

The kinetic energy of the electrons is

$$T = \frac{\hbar^2}{2m_a a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
, and

The energy,  $V_m$ , of the magnetic force between the electrons is

$$V_m = \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
, and

15 The total energy,  $E_T$ , is given by the sum of the energy terms:

$$E_T = V_e + T + V_m + V_n$$

$$E_{T} = -\frac{e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}} \left[ \left(2 - \frac{a_{o}}{a}\right) \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right] = -\frac{e^{2}}{8\pi\varepsilon_{o}c'} \left[ \left(2 - \frac{a_{o}}{a}\right) \ln \frac{a + c'}{a - c'} - 1 \right].$$

54. The system of claim 53 wherein during bond formation, the electrons undergo a reentrant 20 oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar \sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_{T} = -\left\{\frac{e^{2}}{8\pi\varepsilon_{0}c'}\left[\left(2 - \frac{a_{0}}{a}\right)\ln\frac{a + c'}{a - c'} - 1\right]\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$

- 55. The system of claim 54 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{ox}$  is the
- 5 difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$
, and

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_{T} = -\left\{ \frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ \left(2 - \frac{a_{0}}{a}\right) \ln \frac{a+c'}{a-c'} - 1 \right] \left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{e^{2}}{4\pi\varepsilon_{o}b^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right] \right\}$$

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- 56. The system of claim 55 wherein the energy of the MO is matched to that of the outermost atomic orbital of a bonding heteroatom in the case where a minimum energy is achieved with a direct bond to the AO.
- 15 57. The system of claim 56 wherein the MO is continuous with the AO containing paired electrons that do not participate in the bond, and said paired electrons provide a means for the energy matched MO to form a continuous equipotential energy surface.
- 58. The system of claim 57 wherein an independent MO is formed such that the AO force 20 balance causes the remaining electrons to be at lower energy and a smaller radius.
  - 59. The system of claim 58 wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum.

60. The system of claim 59 wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum.

5

- 61. The system of claim 60 wherein at least two atomic orbitals hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals.
  - 62. The system of claim 61 where the force constant k' of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{c_1 c_2 2e^2}{4\pi\varepsilon_a}$$

- where  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie and  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond.
- 63. The system of claim 62 where the distance from the origin of the MO to each focus c' is 20 given by:

$$c' = a \sqrt{\frac{\hbar^2 4\pi \varepsilon_0}{m_e e^2 2k' a}} = \sqrt{\frac{aa_0}{2k'}};$$

the internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2k'}};$$

the length of the semiminor axis of the prolate spheroidal MO b = c is given by

25 
$$b = \sqrt{a^2 - c'^2}$$
, and

and, the eccentricity, e, is

$$e=\frac{c'}{a}$$
.

64. The system of claim 63 wherein the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi \varepsilon_a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}};$$

The potential energy of the two nuclei is

$$V_p = n_1 \frac{e^2}{8\pi\varepsilon_o \sqrt{\alpha^2 - b^2}};$$

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
, and

The energy,  $V_m$ , of the magnetic force between the electrons is

$$V_m = n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
, and

10 The total energy,  $E_T$ , is given by the sum of the energy terms:

$$E_T = V_e + T + V_m + V_p$$

$$E_{T} = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right]$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right]$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie, and  $c_2$  is the factor that

- 15 results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.
  - 65. The system of claim 64 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the
- 20 difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{asc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1 \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_{T} = -\left\{ \frac{n_{1}e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_{1}c_{2}e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - n_{1}\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\}$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie, and  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic 5 orbitals of each chemical bond.

66. The system of claim 65 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{ox}$  is the difference between the Doppler and average vibrational kinetic energies:

10 
$$\overline{E}_{asc} = \overline{E}_D + \overline{E}_{Kwib} = \left(V_e + T + V_m + V_p\right) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1 \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}$$
, and

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_{T} = -\left\{ \frac{n_{e}e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right) \ln\frac{a + c'}{a - c'} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_{1}c_{2}e^{2}}{4\pi\varepsilon_{o}b^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - n_{1}\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\}$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie, and  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

- 67. The system of claim 66 wherein a hybridized shell comprises a linear combination of the 20 electrons of at least two atomic-orbital shells.
  - 68. The system of claim 67 wherein the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for

each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons.

- 69. The system of claim 68 wherein the total energy E<sub>T</sub> (atom, msp³) (m is the integer of the
  5 valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least two AO shells
  - 70. The system of claim 69 wherein the radius  $r_{msp^3}$  of the hybridized shell is given by:

10 
$$r_{msp^3} = \sum_{q=Z-n}^{Z-1} \frac{(Z-q)e^2}{8\pi\varepsilon_0 E_T \left(atom, msp^3\right)}$$

71. The system of claim 70 wherein the Coulombic energy  $E_{Coulomb}$  (atom,  $msp^3$ ) of the outer electron of the atom  $msp^3$  shell is given by

$$E_{Coulomb}\left(atom, msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}}$$

15

72. The system of claim 71 wherein the during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO) and the energy change the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius  $r_n$  of the AO electron:

20 
$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2(r_n)^3} = \frac{8\pi\mu_o\mu_B^2}{(r_n)^3}$$

73. The system of claim 72 wherein the energy  $E(atom, msp^3)$  of the outer electron of the atom  $msp^3$  shell is given by the sum of  $E_{Coulomb}(atom, msp^3)$  and E(magnetic):

$$E(atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(r_{n})^{3}}$$

- 74. The system of claim 73 wherein at least two atomic orbitals hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals; the total energy of the hybridized orbitals is given by the sum of E(atom, msp³) and the next energies of successive ions of the atom over the n electrons comprising total electrons of the at least two initial AO shells; is the sum of the first energy of the atom and the hybridization energy.
- 10 75. The system of claim 74 wherein the sharing of electrons between two *atom msp*<sup>3</sup> HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy.
- 76. The system of claim 75 wherein in order to further satisfy the potential, kinetic, and orbital energy relationships, each atom msp³ HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond.
- 77. The system of claim 76 wherein the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons and the hybridization energy.
- 78. The system of claim 77 wherein the total energy  $E_T$  (mol.atom, msp<sup>3</sup>) (m is the integer of 25 the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least two initial AO shells and the hybridization energy.
  - 79. The system of claim 78 wherein the radius  $r_{max}$ , of the hybridized shell is given by:

30 
$$r_{msp^3} = \left(\sum_{q=Z-n}^{Z-1} (Z-q) - s(0.25)\right) \frac{e^2}{8\pi\varepsilon_0 E_T \left(mol.atom, msp^3\right)}$$

where s = 1, 2, 3 for a single, double, and triple bond, respectively.

80. The system of claim 79 wherein the Coulombic energy  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> shell is given by

5 
$$E_{Coulomb}\left(mol.atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\epsilon_{0}r_{msp^{3}}}$$

81. The system of claim 80 wherein the during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO) and the energy change the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius  $r_n$  of the AO electron:

$$E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_n)^3} = \frac{8\pi\mu_o \mu_B^2}{(r_n)^3}$$

82. The system of claim 81 wherein the energy  $E(mol.atom, msp^3)$  of the outer electron of the atom  $msp^3$  shell is given by the sum of  $E_{Coulomb}(mol.atom, msp^3)$  and E(magnetic):

$$E\left(mol.atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}\left(r_{n}\right)^{3}}$$

83. The system of claim 82 wherein  $E_T(atom-atom,msp^3)$ , the energy change of each atom  $msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(mol.atom,msp^3)$  and  $E(atom,msp^3)$ .

20 
$$E_T(atom-atom, msp^3) = E(mol.atom, msp^3) - E(atom, msp^3)$$

84. The system of claim 83 wherein to meet an energy matching condition for all MOs at all HOs, the energy  $E(mol.atom, msp^3)$  of the outer electron of the atom  $msp^3$  shell of each bonding atom must be the average of  $E(mol.atom, msp^3)$  for two different values of s:

25 
$$E(mol., msp^3) = \frac{E(mol(s_1), msp^3) + E(mol(s_2), msp^3)}{2}$$
 (14.512)

85. The system of claim 84 wherein  $E_T(atom-atom,msp^3)$ , the energy change of each atom  $msp^3$  shell with the formation of each atom-atom-bond MO, is average of  $E_T(atom-atom,msp^3)$  for two different values of s:

5 
$$E_T(atom-atom, msp^3) = \frac{E_T(atom-atom(s_1), msp^3) + E_T(atom-atom(s_2), msp^3)}{2}$$

86. The system of claim 85 wherein the radius  $r_{msp}^3$  of the atom  $msp^3$  shell of each bonding atom is given by the Coulombic energy using the initial energy  $E_{Coulomb}$  (atom,  $msp^3$ ) and  $E_T$  (atom – atom,  $msp^3$ ), the energy change of each atom  $msp^3$  shell with the formation of each atom-atom-bond MO:

$$r_{msp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0}a_{0}\left(E_{Coulonb}\left(atom, msp^{3}\right) + E_{T}\left(atom - atom, msp^{3}\right)\right)}$$
(14.514)

87. The system of claim 86 wherein the Coulombic energy  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> shell is given by

15 
$$E_{Coulomb}\left(mol.atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}}$$

88. The system of claim 87 wherein the during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO) and the energy change the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius  $r_n$  of the AO electron:

$$E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_n)^3} = \frac{8\pi\mu_o \mu_B^2}{(r_n)^3}.$$

25 89. The system of claim 88 wherein the energy  $E(mol.atom, msp^3)$  of the outer electron of

the atom  $msp^3$  shell is given by the sum of  $E_{Coulomb}$  (mol.atom,  $msp^3$ ) and E(magnetic):

$$E(mol.atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(r_{n})^{3}}$$

- 90. The system of claim 89 wherein  $E_T(atom-atom, msp^3)$ , the energy change of each
- 5 atom  $msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(mol.atom, msp^3)$  and  $E(atom, msp^3)$ .

$$E_T(atom-atom, msp^3) = E(mol.atom, msp^3) - E(atom, msp^3)$$

- 91. The system of claim 90 wherein  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) is one of is one of
- 10  $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$ ,  $E_{Coulomb}\left(C_{ethane}, 2sp^3\right)$ ,  $E_{Coulomb}\left(C_{acetylene}, 2sp^3\right)$ , and  $E_{Coulomb}\left(C_{alkane}, 2sp^3\right)$ ;

$$E_{Coulomb}(atom, msp^3)$$
 is one of  $E_{Coulomb}(C, 2sp^3)$  and  $E_{Coulomb}(Cl, 3sp^3)$ ;

$$E(mol.atom, msp^3)$$
 is one of  $E(C_{ethylene}, 2sp^3)$ ,  $E(C_{ethane}, 2sp^3)$ ,

$$E(C_{acetylene}, 2sp^3) E(C_{alkane}, 2sp^3);$$

15  $E(atom, msp^3)$  is one of and  $E(C, 2sp^3)$  and  $E(Cl, 3sp^3)$ ;

$$E_T(atom-atom, msp^3)$$
 is one of  $E(C-C, 2sp^3)$ ,  $E(C=C, 2sp^3)$ , and.

$$E(C \equiv C, 2sp^3);$$

atom msp<sup>3</sup> is one of C2sp<sup>3</sup>, Cl3sp<sup>3</sup>

$$E_T(atom-atom(s_1), msp^3)$$
 is  $E_T(C-C, 2sp^3)$  and  $E_T(atom-atom(s_2), msp^3)$  is

20  $E_T(C = C, 2sp^3)$ , and

$$r_{msp^3}$$
 is one of  $r_{C2sp^3}$ ,  $r_{ethane2sp^3}$ ,  $r_{ethylene2sp^3}$ ,  $r_{acetylene2sp^3}$ ,  $r_{alkane2sp^3}$ , and  $r_{Cl3sp^3}$ ,

- 92. The system of claim 91 wherein the energy of the MO is matched to that of the outermost atomic orbital or hybridized orbital of a bonding atom in the case where a minimum energy is
- 25 achieved with a direct bond to the AO or HO.

93. The system of claim 92 wherein the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_c \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}};$$

5 The potential energy of the two nuclei is

$$V_p = n_1 \frac{e^2}{8\pi\varepsilon_a \sqrt{a^2 - b^2}};$$

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_2 a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
, and

The energy,  $V_m$ , of the magnetic force between the electrons is

10 
$$V_m = n_1 c_1 c_2 \frac{-\dot{n}^2}{4m_a a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}, \text{ and}$$

The total energy,  $E_T$ , is given by the sum of the energy terms plus E(AO):

$$E_T = V_e + T + V_m + V_p$$

$$E_{T} = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right] + E(AO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E(AO)$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type 15 ellipsoidal MO basis function of a chemical bond of the specie,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of

each chemical bond, and E(AO) is the energy of the at least one atomic orbital to which the

MO is energy matched.

20 94. The system of claim 93 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}$$
 , and

the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc} + E(AO).$$

95. The system of claim 94 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{ox}$  is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1 \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} , \text{ and }$$

the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{ost}$$

$$10 \quad E_{T} = -\left\{ \frac{n_{1}e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_{1}c_{2}e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - n_{1} \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\} + E(AO)$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and E(AO) is the energy of the at least one atomic orbital to which the MO is energy matched.

96. The system of claim 95 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\bar{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

20 
$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = (V_e + T + V_m + V_p) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1 \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}$$
, and

the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_{T} = -\left\{ \frac{n_{1}e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_{1}c_{2}e^{2}}{4\pi\varepsilon_{0}b^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - n_{1}\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\} + E(AO)$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and E(AO) is the energy of the at least one atomic orbital or hybridized atomic orbital or said orbital or hybridized orbital and the energy change with the formation of the bond by one or more of the orbital electrons to match the energies of the said orbital and the MO.

10 97. The system of claim 96 wherein E(AO), the energy of the at least one atomic orbital or hybridized atomic orbital or said orbital or hybridized orbital and the energy change with the formation of the bond by one or more of the orbital electrons to match the energies of the said orbital and the MO, is at least one from the group of

$$E(AO) = E(O2p \text{ shell}) = -E(\text{ionization}; O) = -13.6181 \text{ eV};$$

15 
$$E(AO) = E(N2p \text{ shell}) = -E(\text{ionization}; N) = -14.53414 \text{ eV};$$

$$E(AO) = E(C, 2sp^3) = -14.63489 \ eV;$$

$$E_T(AO) = E_{Coulomb}(Cl, 3sp^3) = -14.60295 \ eV;$$

$$E_T(AO) = E(ionization; C) + E(ionization; C^+);$$

$$E_T(AO) = E(C_{ethane}, 2sp^3) = -15.35946 \ eV;$$

20 
$$E_T(AO) = +E(C_{ethylene}, 2sp^3) - E(C_{ethylene}, 2sp^3);$$

$$E_T(AO) = E(C, 2sp^3) - 2E_T(C = C, 2sp^3) = -14.63489 \ eV - (-2.26758 \ eV);$$

$$E_T(AO) = E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) = 16.20002 \text{ eV};$$

$$E_T(AO) = E(C, 2sp^3) - 2E_T(C \equiv C, 2sp^3) = -14.63489 \ eV - (-3.13026 \ eV);$$

$$E_T(AO) = E(C_{benzene}, 2sp^3) - E(C_{benzene}, 2sp^3);$$

 $E_T(AO) = E\left(C,2sp^3\right) - E_T\left(C = C,2sp^3\right) = -14.63489 \ eV - \left(-1.13379 \ eV\right), \text{ and}$   $E_T\left(AO\right) = E\left(C_{alkane},2sp^3\right) = -15.56407 \ eV, \text{ wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to <math>\pm$  10%, if desired.

5

98. The system of claim 97 wherein  $c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2k'a}} = \sqrt{\frac{aa_0}{2k'}}$  is substituted into  $E_T$  to give

$$E_{T} = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right] + E(AO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E(AO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{\frac{aa_{0}}{2k'}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2k'}}}{a - \sqrt{\frac{aa_{0}}{2k'}}} - 1 \right] + E(AO)$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and E(AO) is the energy of the at least one atomic orbital or hybridized atomic orbital to which the MO is energy matched.

- 99. The system of claim 98 wherein  $E(basis\ energies)$  is given by the sum of a first integer  $q_1$  times the total energy of  $H_2$  and a second integer  $q_2$  times the total energy of H, minus a third integer  $q_3$  times the total energy of E(AO) where the first integer can be 1,2,3..., and each of the second and third integers can be 0,1,2,3....
- 100. The system of claim 99 wherein  $E_T$  is set equal to  $E(basis\ energies)$ , and the 20 semimajor axis a is solved.
  - 101. The system of claim 100 wherein the semimajor axis a is solved from the equation of the form:

$$E_{T} = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right] + E(AO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c^{1}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c^{1}}{a - c^{1}} - 1 \right] + E(AO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{\frac{aa_{0}}{2k^{1}}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2k^{1}}}}{a - \sqrt{\frac{aa_{0}}{2k^{1}}}} - 1 \right] + E(AO) = E(basis\ energies)$$

- 102. The system of claims 101 and 63 wherein the distance from the origin of the  $H_2$ -type5 ellipsoidal-MO to each focus c', the internuclear distance 2c', and the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO b=c are solved from the semimajor axis a.
- 103. The system of claims 102 where the number of equivalent bonds of the MO  $n_1$  each 10 comprising an  $H_2$ -type ellipsoidal MO is an integer greater than one.
  - 104. The system of claims 103 where the fraction  $c_1$  of a  $H_2$ -type ellipsoidal MO is 1. 0.75, 0.5, and 0.75/2.
- 15 105. The system of claims 104 where the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO is given by one of the list of 1 and the ratio of the ionization energy of at least one atom of the bond and 13.605804 eV, the Coulombic energy between the electron and proton of H to meet the equipotential condition of the union of the  $H_2$ -type-ellipsoidal-MO and the AO of the atom, wherein the calculated and measured values and constants recited in the equations herein can 20 be adjusted, for example, up to  $\pm$  10%, if desired.
  - 106. The system of claim 105 where the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO is 0.936127, the ratio of the ionization energy of N 14.53414 eV and 13.605804 eV, the Coulombic energy between the electron and proton of H;

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0.91771, the ratio of 14.82575 eV,  $E_{Coulomb}\left(C,2sp^3\right)$  and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.93172, the ratio of 14.60295 eV,  $E_{Coulomb}(Cl, 3sp^3)$  given by Eq. (13.759), and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.87495, the ratio of 15.55033~eV,  $E_{Coulomb}\left(C_{ethane}, 2sp^3\right)$  and 13.605804~eV, the Coulombic energy between the electron and proton of H;

0.85252, the ratio of 15.95955~eV,  $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$  and 13.605804~eV, the Coulombic energy between the electron and proton of H;

0.85252, the ratio of 15.95955~eV,  $E_{Coulomb}\left(C_{benzene},2sp^3\right)$  and 13.605804~eV, the 10 Coulombic energy between the electron and proton of H, or

0.86359, the ratio of 15.55033~eV,  $E_{Coulomb}\left(C_{alkane},2sp^3\right)$  and 13.605804~eV, the Coulombic energy between the electron and proton of H, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

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- 107. The system of claim 106 where the fraction  $c_1$  of a  $H_2$ -type ellipsoidal MO is such that the orbital energy E for each elliptical cross section of the prolate spheroidal MO is given by the sum of the kinetic T and potential V energies; E = T + V is constant; the orbit is closed such that  $T \triangleleft V \mid$ ; the time average of the kinetic energy,  $\langle T \rangle$ , for elliptic motion 20 in an inverse-squared field is 1/2 that of the time average of the magnitude of the potential energy,  $|\langle V \rangle|$  ( $\langle T \rangle = 1/2 |\langle V \rangle|$ ), and in the case that the energy of the MO is matched to at least one atomic orbital (AO), E = T + V, and for all points on the AO, |E| = T = 1/2 |V|.
- 108. The system of claim 107 where the energy of the MO is matched to at least one 25 atomic orbital (AO) such that E = T + V, and for all points on the AO, |E| = T = 1/2|V|.
- 109. A system of claim 108 of computing and rendering the nature of bound atomic and atomic ionic electrons from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations
  30 using a constraint that the bound electron(s) does not radiate under acceleration, comprising:

processing means for processing and solving the equations for charge, mass, and current density functions of electron(s) in a selected atom or ion, wherein the equations are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration; and

- a display in communication with the processing means for displaying the current and charge density representation of the electron(s) of the selected atom or ion.
- 110. The system of claim 109 wherein the physical, Maxwellian solutions of the charge, 10 mass, and current density functions of atoms and atomic ions comprises a solution of the classical wave equation  $\left[\nabla^2 \frac{1}{v^2} \frac{\delta^2}{\delta t^2}\right] \rho(r,\theta,\phi,t) = 0$  which is the equation of motion of the charge.
- 111. The system of claim 110, wherein the time, radial, and angular solutions of the wave equation are separable.
  - 112. The system of claim 111, wherein the boundary constraint of the wave equation solution is nonradiation according to Maxwell's equations.
- 20 113. The system of claim 112, wherein a radial function that satisfies the boundary condition is a radial delta function

$$f(r) = \frac{1}{r^2} \delta(r - r_n).$$

114. The system of claim 113, wherein the boundary condition is met for a time harmonic25 function when the relationship between an allowed radius and the electron wavelength is given by

$$2\pi r_n = \lambda_n,$$

$$\omega = \frac{\hbar}{m_e r^2}, \text{ and}$$

$$v = \frac{\hbar}{m_e r}$$

where  $\omega$  is the angular velocity of each point on the electron surface,  $\nu$  is the velocity of each point on the electron surface, and r is the radius of the electron.

- 115. The system of claim 114, wherein the spin function is given by the uniform function 5  $Y_0^0(\phi,\theta)$  comprising angular momentum components of  $\mathbf{L}_{xy} = \frac{\hbar}{4}$  and  $\mathbf{L}_z = \frac{\hbar}{2}$ .
- 116. The system of claim 115, wherein the atomic and atomic ionic charge and current density functions of bound electrons are described by a charge-density (mass-density) function which is the product of a radial delta function, two angular functions (spherical harmonic functions), and a time harmonic function:

$$\rho(r,\theta,\phi,t) = f(r)A(\theta,\phi,t) = \frac{1}{r^2}\delta(r-r_n)A(\theta,\phi,t); \qquad A(\theta,\phi,t) = Y(\theta,\phi)k(t)$$

wherein the spherical harmonic functions correspond to a traveling charge density wave confined to the spherical shell which gives rise to the phenomenon of orbital angular momentum.

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117. The system of claim 116, wherein based on the radial solution, the angular charge and current-density functions of the electron,  $A(\theta, \phi, t)$ , must be a solution of the wave equation in two dimensions (plus time),

$$\left[\nabla^2 - \frac{1}{v^2} \frac{\delta^2}{\delta t^2}\right] A(\theta, \phi, t) = 0$$

20 where  $\rho(r,\theta,\phi,t) = f(r)A(\theta,\phi,t) = \frac{1}{r^2}\delta(r-r_n)A(\theta,\phi,t)$  and  $A(\theta,\phi,t) = Y(\theta,\phi)k(t)$ 

$$\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi} + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta} - \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\right]A(\theta,\phi,t) = 0$$

where  $\nu$  is the linear velocity of the electron.

118. The system of claim 117, wherein the charge-density functions including the time-25 function factor are

$$\rho(r,\theta,\phi,t) = \frac{e}{8\pi r^2} \left[\delta(r-r_n)\right] \left[Y_0^0(\theta,\phi) + Y_\ell^m(\theta,\phi)\right]$$

 $l \neq 0$ 

$$\rho(r,\theta,\phi,t) = \frac{e}{4\pi r^2} \left[\delta(r-r_n)\right] \left[ Y_0^0(\theta,\phi) + \operatorname{Re}\left\{ Y_t^m(\theta,\phi)e^{i\omega_n t} \right\} \right]$$

where  $Y_{\ell}^{m}(\theta,\phi)$  are the spherical harmonic functions that spin about the z-axis with angular frequency  $\omega_{n}$  with  $Y_{0}^{0}(\theta,\phi)$  the constant function

 $\operatorname{Re}\left\{Y_{\ell}^{m}\left(\theta,\phi\right)e^{i\omega_{n}t}\right\}=P_{\ell}^{m}\left(\cos\theta\right)\cos\left(m\phi+\omega_{n}t\right)\text{ where to keep the form of the spherical}$ 10 harmonic as a traveling wave about the z-axis,  $\omega_{n}=m\omega_{n}$ .

119. The system of claim 118, wherein the spin and angular moment of inertia, I, angular momentum, L, and energy, E, for quantum number 1 are given by

$$l = 0$$

15

$$I_z = I_{spin} = \frac{m_e r_n^2}{2}$$

$$L_z = I\omega \mathbf{i}_z = \pm \frac{\hbar}{2}$$

$$E_{rotational} = E_{rotational, spin} = \frac{1}{2} \left[ I_{spin} \left( \frac{\hbar}{m_e r_n^2} \right)^2 \right] = \frac{1}{2} \left[ \frac{m_e r_n^2}{2} \left( \frac{\hbar}{m_e r_n^2} \right)^2 \right] = \frac{1}{4} \left[ \frac{\hbar^2}{2I_{spin}} \right]$$

20  $l \neq 0$ 

$$I_{orbital} = m_e r_n^2 \left[ \frac{\ell(\ell+1)}{\ell^2 + \ell + 1} \right]^{\frac{1}{2}}$$

$$L_{\varepsilon} = m\hbar$$

$$L_{\rm z~total} = L_{\rm z~spin} + L_{\rm z~orbital}$$

$$E_{rotational, orbital} = \frac{\hbar^2}{2I} \left[ \frac{\ell(\ell+1)}{\ell^2 + 2\ell + 1} \right]$$

$$T = \frac{\hbar^2}{2m_e r_n^2}$$

$$\langle E_{rotational, orbital} \rangle = 0.$$

5 120. The system of claim 119, wherein the force balance equation for one-electron atoms and ions is

$$\frac{m_e}{4\pi r_1^2} \frac{{v_1}^2}{r_1} = \frac{e}{4\pi r_1^2} \frac{Ze}{4\pi \varepsilon_o r_1^2} - \frac{1}{4\pi r_1^2} \frac{\hbar^2}{m_p r_n^3}$$
$$r_1 = \frac{a_H}{Z}$$

where  $a_H$  is the radius of the hydrogen atom.

10

121. The system of claim 120, wherein from Maxwell's equations, the potential energy V, kinetic energy T, electric energy or binding energy  $E_{ele}$  are

$$V = \frac{-Ze^2}{4\pi\varepsilon_o r_1} = \frac{-Z^2e^2}{4\pi\varepsilon_o a_H} = -Z^2 X \ 4.3675 X \ 10^{-18} J = -Z^2 X \ 27.2 \ eV$$

$$T = \frac{Z^2e^2}{8\pi\varepsilon_o a_H} = Z^2 X \ 13.59 \ eV$$

15 
$$T = E_{ele} = -\frac{1}{2} \varepsilon_o \int_{\infty}^{\eta} \mathbf{E}^2 dv \text{ where } \mathbf{E} = -\frac{Ze}{4\pi \varepsilon_o r^2}$$

$$E_{ele} = -\frac{Z^2 e^2}{8\pi \varepsilon_o a_H} = -Z^2 X \ 2.1786 X \ 10^{-18} \ J = -Z^2 X \ 13.598 \ eV ,$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

20

122. The system of claim 121, wherein the force balance equation solution of two electron atoms is a central force balance equation with the nonradiation condition is given by

$$\frac{m_e}{4\pi r_2^2} \frac{v_2^2}{r_2} = \frac{e}{4\pi r_2^2} \frac{(Z-1)e}{4\pi s_0 r_2^2} + \frac{1}{4\pi r_2^2} \frac{\hbar^2}{Zm_e r_2^3} \sqrt{s(s+1)}$$

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which gives the radius of both electrons as

$$r_2 = r_1 = a_0 \left( \frac{1}{Z-1} - \frac{\sqrt{s(s+1)}}{Z(Z-1)} \right); \ s = \frac{1}{2}.$$

123. The system of claim 122, wherein the ionization energy for helium, which has no 5 electric field beyond  $r_1$  is given by

Ionization Energy(He) = -E(electric) + E(magnetic)

where,

$$E(electric) = -\frac{(Z-1)e^2}{8\pi\varepsilon_o r_1}$$

$$E(electric) = -\frac{(Z-1)e^2}{8\pi\varepsilon_o r_1}$$

$$E(magnetic) = \frac{2\pi\mu_0 e^2 h^2}{m_e^2 r_1^3}$$

10 For  $3 \le Z$ 

Ionization Energy = -Electric Energy - 
$$\frac{1}{Z}$$
 Magnetic Energy.

- The system of claim 123, wherein the electrons of multielectron atoms all exist as orbitspheres of discrete radii which are given by  $r_n$  of the radial Dirac delta function,
- 15  $\delta(r-r_n)$ .
  - 125. The system of claim 124, wherein electron orbitspheres may be spin paired or unpaired depending on the force balance which applies to each electron wherein the electron configuration is a minimum of energy.

20

- The system of claim 125, wherein the minimum energy configurations are given by 126. solutions to Laplace's equation.
- 127. The system of claim 126, wherein the electrons of an atom with the same principal 25 and I quantum numbers align parallel until each of the m levels are occupied, and then pairing occurs until each of the m 1 levels contain paired electrons.

- The system of claim 127, wherein the electron configuration for one through twenty-128. electron atoms that achieves an energy minimum is: 1s < 2s < 2p < 3s < 3p < 4s.
- The system of claim 128, wherein the corresponding force balance of the central 129. 5 Coulombic, paramagnetic, and diamagnetic forces was derived for each n-electron atom that was solved for the radius of each electron.
- 130. The system of claim 129, wherein the central Coulombic force is that of a point charge at the origin since the electron charge-density functions are spherically symmetrical 10 with a time dependence that is nonradiative.
  - The system of claim 130, wherein the ionization energies are obtained using the calculated radii in the determination of the Coulombic and any magnetic energies.
- The system of claim 131, wherein the general equation for the radii of s electrons is 15 132. given by

$$r_{n} = \frac{a_{0}\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right)^{2}} + \frac{\left(\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right)\right)^{2}}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right)^{2}} + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]Er_{m}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right)}$$

$$r_{n} \text{ in units of } a_{0}$$

where positive root must be taken in order that  $r_n > 0$ ;

Z is the nuclear charge, n is the number of electrons,

20  $r_m$  is the radius of the proceeding filled shell(s) given by

$$a_{0}\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right) = \begin{bmatrix} \left(1+(C-D)\frac{\sqrt{3}}{2Z}\right) \\ \left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right)^{2} \\ + \left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right) \end{bmatrix} + \begin{bmatrix} 20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]Er_{m}\right) \\ + \left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right) \end{bmatrix}$$

 $r_m$  in units of  $a_0$ 

for the preceding s shell(s);

$$\frac{a_{0}}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)^{\pm}a_{0}}\left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)^{2}}+\frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)}$$

r, in units of ao

for the 2p shell, and

$$\frac{a_{0}}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)} \pm a_{0} \left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)} + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)r_{12}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)} + \frac{r_{n}}{2} \qquad r_{n} = \frac{2}{r_{n} \text{ in units of } a_{0}}$$

for the 3p shell;

the parameter A corresponds to the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ :

$$\mathbf{F}_{diamognetic} = -\frac{\hbar^2}{4m_e r_{\rm s}^2 r_{\rm i}} \sqrt{s(s+1)} \mathbf{i}_{\rm r};$$

the parameter B corresponds to the paramagnetic force,  $\mathbf{F}_{mag 2}$ :

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_1 r_4^2} \sqrt{s(s+1)} \mathbf{i}_r;$$

the parameter C corresponds to the diamagnetic force,  $\mathbf{F}_{diamagnetic\ 3}$ :

5 
$$\mathbf{F}_{diamognetic 3} = -\frac{1}{Z} \frac{8\hbar^2}{m_e r_1} \sqrt{s(s+1)} \mathbf{i}_r$$
;

the parameter D corresponds to the paramagnetic force,  $\mathbf{F}_{mag}$ :

$$\mathbf{F}_{mag} = \frac{1}{4\pi r_2^2} \frac{1}{Z} \frac{\hbar^2}{m_e r^3} \sqrt{s(s+1)}$$
, and

the parameter E corresponds to the diamagnetic force,  $\mathbf{F}_{diamagnetic 2}$ , due to a relativistic effect with an electric field for  $r > r_n$ :

10 
$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-3}{Z-2}\right] \frac{r_1 \hbar^2}{m_e r_3^4} 10\sqrt{3/4} \mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-11}{Z-10}\right] \left(1 + \frac{\sqrt{2}}{2}\right) \frac{r_{10}\hbar^2}{m_e r_{11}^4} 10\sqrt{s(s+1)}\mathbf{i}_r$$
, and

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right] \left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right) \frac{r_{18}\hbar^2}{m_e r_n^4} 10\sqrt{s(s+1)}\mathbf{i}_r.$$

\$873\$ wherein the parameters of atoms filling the 1s, 2s, 3s, and 4s orbitals are

Atom Type	Electron Configuration	Ground State Term	Orbital Arrangement of s Electrons (s state)	-	Paramag. Force Factor B	Diamag. Force Factor C	ag.	Force Factor
Neutral 1 e Atom H	1s1	<sup>2</sup> S <sub>1/2</sub>	<u>↑</u> 1s	0	0	0	0	0
Neutral 2 e Atom	1s <sup>2</sup>	<sup>1</sup> S <sub>0</sub>	↑↓ 1s	<b>0</b> .	0	0	1 .	0
He Neutral 3 e Atom	$2s^1$	<sup>2</sup> S <sub>1/2</sub>	<u>↑</u> 2s	1	0	<b>0</b>	0	0
Li Neutral 4 e Atom	$2s^2$	<sup>1</sup> S <sub>0</sub>	$\frac{\uparrow}{2s}$	1	0	0	1	0
Be Neutral 11 e Atom	$1s^22s^22p^63s^1$	<sup>2</sup> S <sub>1/2</sub>	<u>↑</u> 3s	1	0	8	0	0
Na Neutral 12 e Atom	$1s^22s^22p^63s^2$	<sup>1</sup> S <sub>0</sub>	<u>↑</u> ↓ 3s	1	3	12	1	0
Mg Neutral 19 e Atom	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$^2S_{1/2}$	<u>↑</u> 4s	2	0	12	0	0

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			8/4					
<i>K</i> Neutral	1,22,22, 22, 22, 22, 26,4,2	10	<b>1</b>					
20 e	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$\mathcal{S}^0$	<u>↑ ↓</u> 4s	1	3	24	1	0
Atom			10	•	J	27	•	Ü
Ca	•							
1 e Ion	1 e <sup>1</sup>	<sup>2</sup> C	<b>^</b>					
1 0 1011	(	$^{2}S_{1/2}$	<u>↑</u> 1s	0	0	0	0	0
				-			·	·
2 e Ion	$1s^2$	<sup>1</sup> <b>S</b> .	↑ ↓					
·	22	<sup>1</sup> <b>S</b> <sub>0</sub> .	1s	0	0	0	1	0
3 e Ion	$2s^1$	$^{2}S_{1/2}$	<u>↑</u>					
. •			<u>↑</u> 2s	1	0	0	0	1
4 e Ion	$2s^2$	1S <sub>0</sub>	$\frac{\uparrow \downarrow}{2s}$					
			2s	1	0	0	1	1
11 e Ion	$1s^22s^22p^63s^1$	$^{2}S_{1/2}$	1					
			3s	1	4	.8	0	$1+\frac{\sqrt{2}}{2}$
40. 4	2 2 4 2	,	A 1		•			2
12 e lon	$1s^22s^22p^63s^2$	$^{1}S_{0}$		•		•	•	<b></b>
			<b>3</b> 8	i	O	U	U	$1 + \frac{\sqrt{2}}{2}$
10 a Ton	1.20.20.62.22.64.1	2 cr	<b>^</b>	•				2
	18-28-2p-38-3p-48-	-S <sub>1/2</sub>		3	0	24	0	2 5
			- <b>: :</b>	J	J	<b>∠</b> ¬	v	2-12
20 e Ion	$1s^2 2s^2 2n^6 3s^2 3n^6 4s^2$	<sup>1</sup> S <sub>2</sub>	<b>↑</b> ↓	,				
		~0	4s	2	0	24	0	$2-\sqrt{2}$
12 e Ion 19 e Ion	$1s^{2}2s^{2}2p^{6}3s^{1}$ $1s^{2}2s^{2}2p^{6}3s^{2}$ $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{1}$ $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{1}$		$ \begin{array}{c} \uparrow \\ 3s \end{array} $ $ \uparrow \downarrow \\ 4s $ $ \uparrow \downarrow \\ 4s $	3	4 6 0	0 24	0	$1 + \frac{\sqrt{2}}{2}$ $1 + \frac{\sqrt{2}}{2}$ $2 - \sqrt{2}$ $2 - \sqrt{2}$

133. The system of claim 132, with the radii,  $r_n$ , wherein the ionization energy for atoms having an outer s-shell are given by the negative of the electric energy, E(electric), given by:

$$E(Ionization) = -Electric\ Energy = \frac{(Z - (n-1))e^2}{8\pi\varepsilon_o r_n}$$

except that minor corrections due to the magnetic energy must be included in cases wherein the s electron does not couple to p electrons as given by

Ionization Energy(He) = 
$$-E(electric) + E(magnetic) \left(1 - \frac{1}{2} \left(\frac{2}{3} \cos \frac{\pi}{3}\right)^2 + \alpha\right)\right)$$

5 Ionization Energy = -Electric Energy  $-\frac{1}{Z}$  Magnetic Energy

$$E(ionization; Li) = \frac{(Z-2)e^2}{8\pi\varepsilon_o r_3} + \Delta E_{mag}$$
  
= 5.3178 eV + 0.0860 eV = 5.4038 eV

 $E(Ionization) = E(Electric) + E_{\tau}$ 

$$\begin{split} E(ionization; \ Be) &= \frac{(Z-3)e^2}{8\pi\varepsilon_o r_4} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_4^3} + \Delta E_{mag} \\ &= 8.9216 \ eV + 0.03226 \ eV + 0.33040 \ eV = 9.28430 \ eV \end{split} \ , \ \text{and}$$

 $E(Ionization) = -Electric \ Energy - \frac{1}{Z} Magnetic \ Energy - E_T$ , wherein the calculated and

- 10 measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.
  - 134. The system of claim 133, wherein the radii and energies of the 2p electrons are solved using the forces given by

15 
$$\mathbf{F}_{ele} = \frac{(Z-n)e^2}{4\pi\varepsilon_o r_n^2} \mathbf{i}_r$$

$$\mathbf{F}_{diamognetic} = -\sum_{m} \frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \frac{\hbar^{2}}{4m_{e}r_{e}^{2}r_{3}} \sqrt{s(s+1)} \mathbf{i}_{r}$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{\hbar^2}{m r^2 r} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{\hbar^2}{m_r^2 r_2} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{diamognetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right] \left(1-\frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_n^4} 10\sqrt{s(s+1)} \mathbf{i}_r,$$

and the radii  $r_3$  are given by

$$r_{4} = r_{3} = \frac{\left(2 - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}}{\left(2 - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}} - \frac{\left[\frac{Z - 3}{Z - 2}\right] r_{1} 10 \sqrt{\frac{3}{4}}}{\left(Z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}} - \frac{\left(Z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}}{2}$$

r, in units of a

5 135. The system of claim 134, wherein the electric energy given by

$$E(Ionization) = -Electric \ Energy = \frac{(Z - (n-1))e^2}{8\pi\varepsilon_o r_n}$$

gives the corresponding ionization energies.

136. The system of claim 135, wherein for each n-electron atom having a central charge of

10 Z times that of the proton and an electron configuration  $1s^2 2s^2 2p^{n-4}$ , there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by:

$$r_1 = r_2 = a_o \left[ \frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right];$$

two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by:

$$r_{4} = r_{3} = \frac{\left(2 - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}}{\left(2 - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}} + 4 \frac{\left[\frac{Z - 3}{Z - 2}\right] r_{1} 10 \sqrt{\frac{3}{4}}}{\left(Z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}}\right)}$$

 $r_1$  in units of  $a_o$ 

and n-4 electrons in an orbitsphere with radius  $r_n$  given by

$$\frac{a_{0}}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)^{\pm}a_{0}} + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)};$$

$$r_{n} = \frac{2}{r_{3} \text{ in units of } a_{0}}$$

the positive root must be taken in order that  $r_n > 0$ ;

the parameter A corresponds to the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ :

$$\mathbf{F}_{diamagnetic} = -\sum_{m} \frac{\left(\ell + |m|\right)!}{\left(2\ell + 1\right)\left(\ell - |m|\right)!} \frac{\hbar^2}{4m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}};$$

and the parameter  $\it B$  corresponds to the paramagnetic force,  $\rm F_{\it mag~2}$  :

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_e^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
,

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
, and

5 
$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{\hbar^2}{m_r r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$

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wherein the parameters of five through ten-electron atoms are								
Atom Type	Electron	Ground	Orbital	Diama Param				
	Configuration	State	Arrangement	gnetic	agneti			
		Term	of	Force	c			
			2p Electrons	Factor	Force			
			(2p state)	A	Factor			
					В			
Neutral 5 e Atom  B	$1s^22s^22p^1$	$^{2}P_{1/2}^{0}$	$\frac{\uparrow}{1} - {0} - {-1}$	2	0			
Neutral 6 e Atom	$1s^22s^22p^2$	<sup>3</sup> P <sub>0</sub>	$\frac{\uparrow}{1}$ $\frac{\uparrow}{0}$ ${-1}$	$\frac{2}{3}$	0			
Noutral 7 a Atom	1.20.20.3	4 00	<b>^ ^ ^</b>	1				
N N	15" 25" 2 p"	S <sub>3/2</sub>	$\begin{array}{c c} \uparrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array}$	3	1			
Neutral 8 e Atom	1-22-22-4	3 p	<b>↑                                    </b>					
O O	18 28 2p	<i>I</i> <sub>2</sub>	$\begin{array}{cccc} \uparrow & \downarrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 & \\ \end{array}$	1	2			
Neutral 9 e Atom	$1s^22s^22p^5$	$^{2}P_{3/2}^{0}$	$\begin{array}{cccc} \uparrow & \downarrow & \uparrow & \downarrow & \uparrow \\ \hline 1 & 0 & -1 & \\ \end{array}$	$\frac{2}{3}$	3			
Neutral 10 e Atom Ne	$1s^22s^22p^6$	${}^{1}S_{0}$	$\begin{array}{cccc} \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \downarrow \\ 1 & 0 & -1 & & \\ \end{array}$	0	3			
5 e Ion	$1s^22s^22p^1$	$^{2}P_{1/2}^{0}$	<u>↑</u>	<u>5</u>	1			
6 e Ion	$1s^22s^22p^2$	$^{3}P_{0}$	$\frac{\uparrow}{1}$ $\frac{\uparrow}{0}$ ${-1}$	<u>5</u>	4			
7 e Ion	$1s^2 2s^2 2p^3$	$^{4}S_{3/2}^{0}$	$\begin{array}{c c} \uparrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array}$	$\frac{5}{3}$	6			

8 e Ion 
$$1s^2 2s^2 2p^4$$
  ${}^3P_2$   $\frac{\uparrow}{1}$   $\frac{\uparrow}{0}$   $\frac{\uparrow}{-1}$   $\frac{5}{3}$  6

9 e Ion 
$$1s^2 2s^2 2p^5$$
  ${}^2P_{3/2}^0$   $\frac{\uparrow}{1}$   $\frac{\uparrow}{0}$   $\frac{\uparrow}{-1}$   $\frac{5}{3}$  9

137. The system of claim 136, wherein the ionization energy for the boron atom is given by

$$E(ionization; B) = \frac{(Z-4)e^2}{8\pi\varepsilon_o r_s} + \Delta E_{mag}$$
$$= 8.147170901 \ eV + 0.15548501 \ eV = 8.30265592 \ eV$$

- 5 wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.
- 138. The system of claim 137, wherein the ionization energies for the n-electron atoms 10 having the radii,  $r_n$ , are given by the negative of the electric energy, E(electric), given by

$$E(Ionization) = -Electric \ Energy = \frac{(Z - (n-1))e^2}{8\pi\varepsilon_0 r_n}.$$

139. The system of claim 138, wherein the radii of the 3p electrons are given using the forces given by

15 
$$\mathbf{F}_{ele} = \frac{(Z-n)e^2}{4\pi\varepsilon_o r_n^2} \mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\sum_{m} \frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \frac{\hbar^{2}}{4m_{e}r_{n}^{2}r_{12}} \sqrt{s(s+1)}\mathbf{i}_{r}$$

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right) \frac{\hbar^2}{4m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r = -\left(\frac{5}{3}\right) \frac{\hbar^2}{4m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mog 2} = \left(4 + 4 + 4\right) \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r = \frac{1}{Z} \frac{12\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{4\hbar^2}{m_r^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{4\hbar^2}{m_r^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

5 
$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{8\hbar^2}{m_r r_s^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

and the radii  $r_{12}$  are given by

$$r_{12} = \frac{a_0}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)^2} \pm a_0 \sqrt{\frac{1}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)^2}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}}$$

 $r_{10}$  in units of  $a_0$ 

140. The system of claim 139, wherein the ionization energies are given by electric energy 10 given by:

$$E(Ionization) = -Electric \ Energy = \frac{(Z - (n-1))e^2}{8\pi\varepsilon_r r_n}.$$

141. The system of claim 140, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>n-12</sup>, there are two
 15 indistinguishable spin-paired electrons in an orbitsphere with radii r<sub>1</sub> and r<sub>2</sub> both given by:

$$r_1 = r_2 = a_o \left[ \frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right]$$

two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by:

$$r_{4} = r_{3} = \frac{\left(\frac{\sqrt{\frac{3}{4}}}{2}\right)}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)} \left(\frac{\left(\frac{1-\sqrt{\frac{3}{4}}}{Z}\right)^{2}}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)^{2} + 4\frac{\left[\frac{Z-3}{Z-2}\right]r_{1}10\sqrt{\frac{3}{4}}}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)}\right)}$$

 $r_1$  in units of  $a_o$ 

5 three sets of paired indistinguishable electrons in an orbitsphere with radius  $r_{10}$  given by:

$$r_{10} = \frac{a_0}{\left((Z-9) - \left(\frac{5}{24} - \frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}\right)^2} + \frac{1}{\left((Z-9) - \left(\frac{5}{24} - \frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}\right)} + \frac{20\sqrt{3}\left(\left[\frac{Z-10}{Z-9}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-9) - \left(\frac{5}{24} - \frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}\right)}$$

 $r_3$  in units of  $a_0$ 

two indistinguishable spin-paired electrons in an orbitsphere with radius  $r_{12}$  given by:

$$r_{12} = \frac{a_0}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)^2} + \frac{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)^2}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}$$

 $r_{10}$  in units of  $a_0$ 

and n-12 electrons in a 3p orbitsphere with radius  $r_n$  given by

$$r_{n} = \frac{a_{0}}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)^{2}} + \frac{1}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)} + \frac{20\sqrt{3}\left(\left[\frac{Z - n}{Z - (n-1)}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)r_{12}\right)}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}$$

 $r_{12}$  in units of  $a_0$ 

5 where the positive root must be taken in order that  $r_n > 0$ ;

the parameter A corresponds to the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ :

$$\mathbf{F}_{diamagnetic} = -\sum_{m} \frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \frac{\hbar^2}{4m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r, \text{ and the parameter } B \text{ corresponds to the}$$

paramagnetic force,  $F_{mag 2}$ :

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

10 
$$\mathbf{F}_{mag 2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_s r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_s r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i_r}$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$
, and

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{8\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i_r}$$

885 wherein the parameters of thirteen through eighteen-electron atoms are

Atom Type	Electron Configuration	Ground State Term	Orbital Arrangement of 3p Electrons (3p state)	Diamagn etic Force Factor A	Paramag netic Force Factor B
Atom	$1s^2 2s^2 2p^6 3s^2 3p^1$		,		0
Neutral 14 e Atom Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	$^{3}P_{0}$	$\begin{array}{cccc} \uparrow & \uparrow & \\ \hline 1 & 0 & -1 & \\ \end{array}$	$\frac{7}{3}$	0
	$1s^2 2s^2 2p^6 3s^2 3p^3$	<sup>4</sup> S <sub>3/2</sub>	$\begin{array}{c c} \uparrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array}$	5 3	2
	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^3P_2$	$\begin{array}{cccc} \uparrow & \downarrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 & \\ \end{array}$	4/3	1
	$1s^2 2s^2 2p^6 3s^2 3p^5$	$^{2}P_{3/2}^{0}$	$\begin{array}{cccc} \uparrow & \downarrow & \uparrow & \downarrow & \uparrow \\ 1 & 0 & -1 & \\ \end{array}$	2/3	2
Neutral 18 e Atom	$1s^2 2s^2 2p^6 3s^2 3p^6$	<sup>1</sup> S <sub>0</sub>	$\begin{array}{cccc} \uparrow & \downarrow & \uparrow & \downarrow & \uparrow & \downarrow \\ 1 & 0 & -1 & & & \\ & & & & & & \\ \end{array}$	1/3	4
Ar 13 e Ioi	$1 1s^2 2s^2 2p^6 3s^2 3p^1$	$^{2}P_{1/2}^{0}$	1 0 -1	<u>5</u> 3	12

14 e Ion 
$$1s^2 2s^2 2p^6 3s^2 3p^2$$
  $^{3}P_0$   $\frac{\uparrow}{1}$   $\frac{\uparrow}{0}$   $\frac{1}{3}$  16

15 e Ion 
$$1s^2 2s^2 2p^6 3s^2 3p^3$$
  ${}^4S^0_{3/2}$   $\uparrow$   $\uparrow$   $\uparrow$   $\uparrow$   $\uparrow$   $\downarrow$  1 0 -1 0 24

17 e Ion 
$$1s^2 2s^2 2p^6 3s^2 3p^5$$
  ${}^2P_{3/2}^0$   $\frac{\uparrow}{1}$   $\frac{\uparrow}{0}$   $\frac{\uparrow}{-1}$   $\frac{2}{3}$  32

18 e Ion 
$$1s^2 2s^2 2p^6 3s^2 3p^6$$
  ${}^{1}S_0$   $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow 1$  0 40

142. The system of claim 141, wherein the ionization energies for the n-electron 3p atoms are given by electric energy given by:

$$E(Ionization) = -Electric \ Energy = \frac{(Z - (n-1))e^2}{8\pi\varepsilon_0 r_n}.$$

5

143. The system of claim 142, wherein the ionization energy for the aluminum atom is given by

E(ionization; AI) = 
$$\frac{(Z-12)e^2}{8\pi\varepsilon_o r_{13}} + \Delta E_{mag}$$
  
= 5.95270 eV + 0.031315 eV = 5.98402 eV

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm 10\%$ , if desired.

144. A system of claim 1 of computing the nature of bound atomic and atomic ionic electrons from physical solutions of the charge, mass, and current density functions of atoms

and atomic ions, which solutions are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration, comprising:

processing means for processing and solving the equations for charge, mass, and current density functions of electron(s) in selected atoms or ions, wherein the equations are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration; and

output means for outputting the solutions of the charge, mass, and current density functions of the atoms and atomic ions.

- 10 145. A system of claim 1 comprising the steps of;
  - a.) inputting electron functions that are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration;
    - b.) inputting a trial electron configuration;
- c.) inputting the corresponding centrifugal, Coulombic, diamagnetic and paramagnetic
   forces,
  - d.) forming the force balance equation comprising the centrifugal force equal to the sum of the Coulombic, diamagnetic and paramagnetic forces;
    - e.) solving the force balance equation for the electron radii;
- f.) calculating the energy of the electrons using the radii and the corresponding
   20 electric and magnetic energies;
  - g.) repeating Steps a-f for all possible electron configurations, and
  - h.) outputting the lowest energy configuration and the corresponding electron radii for that configuration.
- 25 146. The system of claim 145, wherein the output is rendered using the electron functions.
  - 147. The system of claim 146, wherein the electron functions are given by at least one of the group comprising:

30 l = 0

$$\rho(r,\theta,\phi,t) = \frac{e}{8\pi r^2} \left[ \delta(r-r_n) \right] \left[ Y_0^0(\theta,\phi) + Y_\ell^m(\theta,\phi) \right]$$

5

$$\rho(r,\theta,\phi,t) = \frac{e}{4\pi r^2} \left[\delta(r-r_n)\right] \left[ Y_0^0(\theta,\phi) + \operatorname{Re}\left\{ Y_t^m(\theta,\phi)e^{i\omega_n t} \right\} \right]$$

where  $Y_t^m\left(\theta,\phi\right)$  are the spherical harmonic functions that spin about the z-axis with angular frequency  $\omega_n$  with  $Y_0^0\left(\theta,\phi\right)$  the constant function. Re $\left\{Y_t^m\left(\theta,\phi\right)e^{i\omega_n t}\right\} = P_t^m\left(\cos\theta\right)\cos\left(m\phi + \omega_n t\right)$  where to keep the form of the spherical harmonic as a traveling wave about the z-axis,  $\omega_n = m\omega_n$ .

10 148. The system of claim 147, wherein the forces are given by at least one of the group comprising:

$$\mathbf{F}_{ele} = \frac{(Z - n)e^2}{4\pi\varepsilon_0 r_n^2} \mathbf{i}_r$$

$$\mathbf{F}_{ele} = \frac{(Z - (n-1))e^2}{4\pi\varepsilon_o r_n^2} \mathbf{i}_r$$

$$\mathbf{F}_{mog} = \frac{1}{4\pi r^2} \frac{1}{Z} \frac{\hbar^2}{m r^3} \sqrt{s(s+1)}$$

15 
$$\mathbf{F}_{diamagnetic} = -\frac{\hbar^2}{4m_r r_a^2 r_1} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\sum_{m} \frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \frac{\hbar^2}{4m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\sum_{m} \frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \frac{\hbar^{2}}{4m_{e}r_{n}^{2}r_{12}} \sqrt{s(s+1)}\mathbf{i}_{r}$$

$$\mathbf{F}_{diamognetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right) \frac{\hbar^2}{4m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i_r} = -\left(\frac{5}{3}\right) \frac{\hbar^2}{4m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i_r}$$

$$\mathbf{F}_{diamagnetic 2} = -\left[\frac{Z-3}{Z-2}\right] \frac{r_1 \hbar^2}{m_e r_3^4} 10\sqrt{3/4} \mathbf{i}_r$$

20 
$$\mathbf{F}_{diamognetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right] \left(1-\frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m_e r_n^4} 10\sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z - 11}{Z - 10}\right] \left(1 + \frac{\sqrt{2}}{2}\right) \frac{r_{10}\hbar^2}{m_e r_{11}^4} 10\sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right] \left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right) \frac{r_{18}\hbar^2}{m_e r_n^4} 10\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic 3} = -\frac{1}{Z} \frac{8\hbar^2}{m_o r_{11}^3} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$

5 
$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{\hbar^2}{m.r.r_*^2} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \left(4 + 4 + 4\right) \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r = \frac{1}{Z} \frac{12\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{4\hbar^2}{m_r r_e^2 r_2} \sqrt{s(s+1)} \mathbf{i}_r$$
, and

10 
$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{8\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

149. The system of claim 148, wherein the radii are given by at least one of the group comprising:

$$r_1 = r_2 = a_o \left[ \frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right]$$

$$r_{4} = r_{3} = \frac{\left(Z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right)^{\frac{3}{4}}}{\left(Z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right)^{\frac{3}{4}}} \pm a_{o} \left(\frac{\left(Z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right)^{\frac{3}{4}}}{\left(Z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right)^{\frac{3}{4}}} + 4 \frac{\left[\frac{Z - 3}{Z - 2}\right]r_{1}10\sqrt{\frac{3}{4}}}{\left(Z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right)^{\frac{3}{4}}}\right)}$$

 $r_1$  in units of  $a_0$ 

$$r_{n} = \frac{a_{0}}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)^{\pm} a_{0}} + \frac{1}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)} + \frac{20\sqrt{3}\left(\left[\frac{Z - n}{Z - (n-1)}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)}$$

 $r_3$  in units of  $a_0$ 

$$r_{10} = \frac{a_0}{\left[ (Z-9) - \left( \frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \pm a_0 \left[ \frac{1}{\left[ (Z-9) - \left( \frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} + \frac{20\sqrt{3} \left[ \left[ \frac{Z-10}{Z-9} \right] \left( 1 - \frac{\sqrt{2}}{2} \right) r_3 \right)}{\left[ (Z-9) - \left( \frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \right]}$$

 $r_3$  in units of  $a_0$ 

$$r_{11} = \frac{a_0 \left(1 + \frac{8}{Z} \sqrt{\frac{3}{4}}\right)}{(Z - 10) - \frac{\sqrt{\frac{3}{4}}}{4r_0}}, r_{10} \text{ in units of } a_0$$

$$\frac{a_{0}}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)^{\pm}} + \frac{\left(\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)\right)^{2}}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)} + \frac{20\sqrt{3}\left(\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{Z}\right)r_{10}\right)}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}$$

 $r_{10}$  in units of  $a_0$ 

$$\frac{a_{0}}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)^{\pm}a_{0}} + \frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)^{2}} + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)r_{12}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}$$

 $r_{12}$  in units of  $a_0$ 

$$\frac{a_0 \left(1 + (C - D)\frac{\sqrt{3}}{2Z}\right)}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)^{\frac{1}{2}}} + \frac{20\sqrt{3} \left(\left[\frac{Z - n}{Z - (n-1)}\right] E r_m\right)}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)}$$

$$= \frac{20\sqrt{3} \left(\left[\frac{Z - n}{Z - (n-1)}\right] E r_m\right)}{2} + \frac{20\sqrt{3} \left(\left[\frac{Z - n}{Z - (n-1)}\right] E r_m\right)}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)}$$

 $r_m$  in units of  $a_0$ 

150. The system of claim 149, wherein the electric energy of each electron of radius  $r_n$  is given by at least one of the group comprising:

$$E(electric) = -\frac{(Z - (n-1))e^2}{8\pi\varepsilon_o r_n}$$

5 Ionization Energy(He) = 
$$-E(electric) + E(magnetic) \left(1 - \frac{1}{2} \left(\frac{2}{3} \cos \frac{\pi}{3}\right)^2 + \alpha\right)\right)$$

Ionization Energy = -Electric Energy  $-\frac{1}{Z}$  Magnetic Energy

$$E(Ionization) = -Electric \ Energy - \frac{1}{Z} Magnetic \ Energy - E_T$$

$$E(ionization; Li) = \frac{(Z-2)e^2}{8\pi\varepsilon_o r_3} + \Delta E_{mag}$$

$$=5.3178 \ eV + 0.0860 \ eV = 5.4038 \ eV$$

$$E(ionization; B) = \frac{(Z-4)e^2}{8\pi\varepsilon_o r_5} + \Delta E_{mag}$$

$$= 8.147170901 \, eV + 0.15548501 \, eV = 8.30265592 \, eV$$

10 
$$E(ionization; Be) = \frac{(Z-3)e^2}{8\pi\varepsilon_o r_4} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_4^3} + \Delta E_{mag}$$

$$= 8.9216 \ eV + 0.03226 \ eV + 0.33040 \ eV = 9.28430 \ eV$$

$$(Z - 10)e^{2}$$

E(ionization; Na) = -Electric Energy = 
$$\frac{(Z-10)e^2}{8\pi\varepsilon_o r_{11}}$$
 = 5.12592 eV

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

15 151. The system of claim 150, wherein the radii of s electrons are given by

$$r_{n} = \frac{a_{0}\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right)^{2}} + \frac{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right)^{2}}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right)} + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]Er_{m}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right)}$$

$$r_{n} \text{ in units of } a_{0}$$

where positive root must be taken in order that  $r_n > 0$ ;

Z is the nuclear charge, n is the number of electrons,  $r_m$  is the radius of the proceeding filled shell(s) given by

$$a_{0}\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right) = \left(\frac{\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right)^{2}} + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]Er_{m}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{m}}\right)}$$

$$r_{n} = \frac{20\sqrt{3}\left(\frac{Z-n}{Z-(n-1)}\right)Er_{m}}{2}$$

for the preceding s shell(s);

$$\frac{a_{0}}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)^{\pm}a_{0}} \left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)}\right)^{2}}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)} + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)} - \frac{2}{r_{3} \text{ in units of } a_{0}}$$

for the 2p shell, and

$$r_{n} = \frac{a_{0}}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)^{2}} + \frac{1}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)^{2}} + \frac{20\sqrt{3}\left(\left[\frac{Z - n}{Z - (n-1)}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)r_{12}\right)}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}$$

 $r_{12}$  in units of  $a_0$ 

for the 3p shell;

5 the parameter A corresponds to the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ :

$$\mathbf{F}_{diamagnetic} = -\frac{\hbar^2}{4m_e r_s^2 r_1} \sqrt{s(s+1)} \mathbf{i}_r;$$

the parameter B corresponds to the paramagnetic force,  $\mathbf{F}_{mag\ 2}$ :

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_i r_i^2} \sqrt{s(s+1)} \mathbf{i}_r;$$

the parameter C corresponds to the diamagnetic force,  $\mathbf{F}_{diamagnetic\ 3}$ :

10 
$$\mathbf{F}_{diamagnetic 3} = -\frac{1}{Z} \frac{8\hbar^2}{m_r r_{13}} \sqrt{s(s+1)} \mathbf{i}_r$$
;

the parameter D corresponds to the paramagnetic force,  $\mathbf{F}_{mog}$ :

$$\mathbf{F}_{mag} = \frac{1}{4\pi r_2^2} \frac{1}{Z} \frac{\hbar^2}{m_e r^3} \sqrt{s(s+1)}$$
, and

the parameter E corresponds to the diamagnetic force,  $\mathbf{F}_{diamagnetic\ 2}$ , due to a relativistic effect with an electric field for  $r > r_n$ :

$$\mathbf{F}_{diamagnelic\ 2} = -\left[\frac{Z-3}{Z-2}\right] \frac{r_1 \hbar^2}{m_e r_1^4} 10\sqrt{3/4} \mathbf{i}_r$$

5 
$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-11}{Z-10}\right] \left(1 + \frac{\sqrt{2}}{2}\right) \frac{r_{10}\hbar^2}{m_e r_{11}^4} 10\sqrt{s(s+1)}\mathbf{i}_r$$
, and

$$\mathbf{F}_{diamognetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right] \left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2} - \frac{\sqrt{2}}{2} + \frac{1}{2}\right) \frac{r_{18}\hbar^2}{m_e r_n^4} 10\sqrt{s(s+1)} \mathbf{i}_r.$$

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wherein the parameters of atoms filling the 1s, 2s, 3s, and 4s orbitals are								
Atom	Electron	Ground	Orbital	Dia	Para	Dia	Para	Diamag
Type	Configuration	State	Arrangemen	mag.	mag.	mag.	mag.	•
		Term	t	Forc	Forc	Forc	Forc	Force
			of	e	е	е	e	Factor
			s Electrons	Fact	Fact	Fact	Fact	E
			(s state)	or	or	or	or	
				A	B	$\boldsymbol{C}$	D	
Neutral	1s <sup>1</sup>	$^{2}S_{1/2}$	<u>↑</u>					
1 e			1s	0	0	0	.0	0
Atom						•		
H								
Neutral	1s <sup>2</sup>	<sup>1</sup> S <sub>0</sub>	$\uparrow \downarrow$					-
2 e			1s	0	0	0	1	0
Atom								
Не								
Neutral	$2s^1$	$^{2}S_{1/2}$	<u>↑</u>					
3 e			2s	1	0	0	0	0
Atom								
Li			<b>A</b> 1					
Neutral	$2s^2$	<sup>1</sup> S <sub>0</sub>	<u>↑</u> ↓		•		_	^
4 e			2s	1	0	0	1	0
Atom								
Be	. 2- 2- 6- 1	2						
	$1s^22s^22p^63s^1$	$^{2}S_{1/2}$	3s		^	0	^	0
11 e			38	1	0	8	0	0
Atom								
Na Neutral	1 20.20 60 2	1 <b>c</b>	<b>↑</b> I					
Neutrai 12 e	$1s^22s^22p^63s^2$	<sup>1</sup> S <sub>0</sub>	$\frac{T  \downarrow}{3s}$	1	3	12	1	0
Atom			Jo	1	J	12	1	v
Mg								
MZ								

Neutral  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^{1/2}$ 19 e

4s

2 0 12 0 0

Atom

K

Neutral  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$   $^1S_0$ 20 e

1 3 24 1 0

Atom

Ca

1 e Ion  $1s^1$ 

 $^{2}S_{1/2}$ ls

0 0

0

 $2 e Ion 1s^2$ 

 $^{1}S_{0}$ 

0

 $3 e Ion 2s^1$ 

 $^{2}S_{1/2}$ 2s

1

0

1

 $4 e Ion 2s^2$ 

 $^{1}S_{0}$ 2s

1

0

6

0 1

11 e Ion  $1s^2 2s^2 2p^6 3s^1$ 

 $^{2}S_{1/2}$ 1 3s

1

12 e Ion  $1s^2 2s^2 2p^6 3s^2$ 

 $^{1}S_{0}$ 3s

1

0

19 e Ion  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^{1/2}$ 

3

0 24 0

20 e Ion  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$   $1S_0$ 

 $\uparrow$   $\downarrow$ 4s

2 0 24 0

 $2-\sqrt{2}$ 

152. The system of claim 151, with the radii,  $r_n$ , wherein the ionization energy for atoms having an outer s-shell are given by the negative of the electric energy, E(electric), given by:

$$E(Ionization) = -Electric\ Energy = \frac{(Z - (n-1))e^2}{8\pi\varepsilon_0 r_n}$$

except that minor corrections due to the magnetic energy must be included in cases wherein 5 the s electron does not couple to p electrons as given by

Ionization Energy(He) = 
$$-E(electric) + E(magnetic) \left(1 - \frac{1}{2} \left(\frac{2}{3} \cos \frac{\pi}{3}\right)^2 + \alpha\right)\right)$$

Ionization Energy = -Electric Energy  $-\frac{1}{Z}$  Magnetic Energy

$$E(ionization; Li) = \frac{(Z-2)e^2}{8\pi\epsilon_o r_3} + \Delta E_{mag}$$
  
= 5.3178 eV + 0.0860 eV = 5.4038 eV

 $E(Ionization) = E(Electric) + E_T$ 

$$E(ionization; Be) = \frac{(Z-3)e^2}{8\pi\epsilon_o r_4} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_4^3} + \Delta E_{mog}$$
, and 
$$= 8.9216 \ eV + 0.03226 \ eV + 0.33040 \ eV = 9.28430 \ eV$$

$$E(Ionization) = -Electric \ Energy - \frac{1}{Z} Magnetic \ Energy - E_T$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

15 153. The system of claim 152, wherein the radii and energies of the 2p electrons are solved using the forces given by

$$\mathbf{F}_{ele} = \frac{(Z - n)e^2}{4\pi\varepsilon_o r_n^2} \mathbf{i}_r$$

$$\mathbf{F}_{diamognetic} = -\sum_{m} \frac{\left(\ell + |m|\right)!}{\left(2\ell + 1\right)\left(\ell - |m|\right)!} \frac{\hbar^{2}}{4m_{e}r_{n}^{2}r_{3}} \sqrt{s(s+1)} \mathbf{i}_{r}$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{\hbar^2}{m_r r_p^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$

20 
$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{\hbar^2}{m_s r_s^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right] \left(1-\frac{\sqrt{2}}{2}\right) \frac{r_3\hbar^2}{m_e r_n^4} 10\sqrt{s(s+1)}\mathbf{i}_r,$$

and the radii  $r_3$  are given by

$$r_{4} = r_{3} = \frac{\left(\frac{1-\sqrt{\frac{3}{4}}}{2}\right)}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)}$$

 $r_1$  in units of  $a_0$ 

5

154. The system of claim 153, wherein the electric energy given by

$$E(Ionization) = -Electric\ Energy = \frac{(Z - (n-1))e^2}{8\pi\varepsilon_0 r_n}$$

gives the corresponding ionization energies.

10 155. The system of claim 154, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration  $1s^2 2s^2 2p^{n-4}$ , there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by:

$$r_1 = r_2 = a_o \left[ \frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right];$$

two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by:

$$r_{4} = r_{3} = \frac{\left(\frac{\sqrt{\frac{3}{4}}}{2}\right)}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)} \left(\frac{\left(\frac{\sqrt{\frac{3}{4}}}{Z}\right)^{2}}{\left(\frac{1 - \frac{\sqrt{\frac{3}{4}}}{Z}}{Z}\right)^{2} + 4} \cdot \frac{\left[\frac{Z-3}{Z-2}\right]r_{1}10\sqrt{\frac{3}{4}}}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)}\right)}$$

 $r_1$  in units of  $a_o$ 

5 and n-4 electrons in an orbitsphere with radius  $r_n$  given by

$$\frac{a_{0}}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)^{\pm}a_{0}}\left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)^{2}}+\frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{3}}\right)}\right)}$$

$$r_{n}=\frac{2}{r_{3} \text{ in units of } a_{0}}$$

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the positive root must be taken in order that  $r_n > 0$ ;

the parameter A corresponds to the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ :

$$\mathbf{F}_{diamagnetto} = -\sum_{m} \frac{\left(\ell + \left|m\right|\right)!}{\left(2\ell + 1\right)\left(\ell - \left|m\right|\right)!} \frac{\hbar^{2}}{4m_{e}r_{n}^{2}r_{3}} \sqrt{s(s+1)}\mathbf{i}_{r};$$

and the parameter B corresponds to the paramagnetic force,  $\mathbf{F}_{mag 2}$ :

5 
$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{\hbar^2}{m_c r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
,

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
, and

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$
.

902 wherein the parameters of five through ten-electron atoms are

Atom Type		Term	Arrangement of 2p Electrons (2p state)		
Neutral 5 e Atom B	$1s^2 2s^2 2p^1$	$^{2}P_{1/2}^{0}$	1 0 -1	2	0
Neutral 6 e Atom	$1s^22s^22p^2$	<sup>3</sup> P <sub>0</sub>	$\frac{\uparrow}{1}$ $\frac{\uparrow}{0}$ ${-1}$	$\frac{2}{3}$	0
Neutral 7 e Atom	$1s^22s^22p^3$	$^{4}S_{3/2}^{0}$	$\begin{array}{c c} \uparrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array}$	$\frac{1}{3}$	1
Neutral 8 e Atom	$1s^22s^22p^4$	<sup>3</sup> P <sub>2</sub>	$\begin{array}{cccc} \uparrow & \downarrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 & \\ \end{array}$	1	2
Neutral 9 e Atom	$1s^22s^22p^5$	$^{2}P_{3/2}^{0}$	$\begin{array}{cccc} \uparrow & \downarrow & \uparrow & \downarrow & \uparrow \\ 1 & 0 & -1 & \end{array}$	$\frac{2}{3}$	3
Neutral 10 e Atom	$1s^22s^22p^6$	$^{1}S_{0}$	$\begin{array}{cccc} \uparrow & \downarrow & \uparrow & \downarrow & \uparrow & \downarrow \\ 1 & 0 & -1 & & & \\ \end{array}$	0	3
5 e Ion	$1s^22s^22p^1$	$^{2}P_{1/2}^{0}$	1 0 -1	<u>5</u>	1
6 e Ion	$1s^22s^22p^2$	<sup>3</sup> P <sub>0</sub>	$\frac{\uparrow}{1}$ $\frac{\uparrow}{0}$ ${-1}$	<u>5</u>	4
7 e Ion	$1s^22s^22p^3$	<sup>4</sup> S <sub>3/2</sub>	$\begin{array}{cccc} \uparrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array}$	<u>5</u>	6

8 e Ion 
$$1s^2 2s^2 2p^4$$
  ${}^3P_2$   $\frac{\uparrow}{1}$   $\frac{\uparrow}{0}$   $\frac{\uparrow}{-1}$   $\frac{5}{3}$  6

9 e Ion 
$$1s^2 2s^2 2p^5$$
  ${}^2P_{3/2}^0$   $\frac{\uparrow \downarrow}{1}$   $\frac{\uparrow \downarrow}{0}$   $\frac{\uparrow}{-1}$   $\frac{5}{3}$  9

156. The system of claim 155, wherein the ionization energy for the boron atom is given by

$$E(ionization; B) = \frac{(Z-4)e^2}{8\pi\varepsilon_o r_5} + \Delta E_{mag}$$

$$= 8.147170901 \ eV + 0.15548501 \ eV = 8.30265592 \ eV$$

- 5 wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.
  - 157. The system of claim 156, wherein the ionization energies for the n-electron atoms having the radii,  $r_n$ , are given by the negative of the electric energy, E(electric), given by

10 
$$E(Ionization) = -Electric\ Energy = \frac{(Z - (n-1))e^2}{8\pi\varepsilon_e r_e}$$
.

158. The system of claim 157, wherein the radii of the 3p electrons are given using the forces given by

$$\mathbf{F}_{ele} = \frac{(Z-n)e^2}{4\pi\varepsilon_o r_n^2} \mathbf{i}_r$$

15 
$$\mathbf{F}_{diamagnetic} = -\sum_{m} \frac{(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} \frac{\hbar^{2}}{4m_{e}r_{n}^{2}r_{12}} \sqrt{s(s+1)}\mathbf{i}_{r}$$

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3} + \frac{2}{3} + \frac{1}{3}\right) \frac{\hbar^2}{4m_r r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r = -\left(\frac{5}{3}\right) \frac{\hbar^2}{4m_s r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mag 2} = (4+4+4) \frac{1}{Z} \frac{\hbar^2}{m r_*^2 r_0} \sqrt{s(s+1)} \mathbf{i}_r = \frac{1}{Z} \frac{12\hbar^2}{m r_*^2 r_0} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{4\hbar^2}{m_r^2 r_{12}} \sqrt{s(s+1)} \mathbf{i_r}$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_e^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_{\mathbf{r}}$$

5 
$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{8\hbar^2}{m_r r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

and the radii  $r_{12}$  are given by

$$r_{12} = \frac{a_0}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)^2} + \frac{\left(\frac{1}{(Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)^2}{20\sqrt{3}\left(\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)r_{10}\right)}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}$$

 $r_{10}$  in units of  $a_0$ 

159. The system of claim 158, wherein the ionization energies are given by electric energy 10 given by:

$$E(Ionization) = -Electric Energy = \frac{(Z - (n-1))e^2}{8\pi\varepsilon_n r_n}$$
.

160. The system of claim 159, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration  $1s^22s^22p^63s^23p^{n-12}$ , there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by:

$$r_1 = r_2 = a_0 \left[ \frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right]$$

two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by:

$$r_{4} = r_{3} = \frac{\left(\frac{\sqrt{\frac{3}{4}}}{2}\right)}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)} \left(\frac{\left(\frac{\sqrt{\frac{3}{4}}}{2}\right)^{2}}{\left(\frac{1 - \frac{\sqrt{\frac{3}{4}}}{Z}}{2}\right)^{2} + 4 \cdot \left(\frac{Z-3}{Z-2}\right)r_{1}10\sqrt{\frac{3}{4}}}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)}\right)}$$

 $r_1$  in units of  $a_o$ 

5 three sets of paired indistinguishable electrons in an orbitsphere with radius  $r_{10}$  given by:

$$\frac{a_0}{\left((Z-9)-\left(\frac{5}{24}-\frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}\right)^{\pm}a_0}\begin{pmatrix} \frac{1}{\left((Z-9)-\left(\frac{5}{24}-\frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}\right)^2}{\left((Z-9)-\left(\frac{5}{24}-\frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}\right)} \\ + \frac{20\sqrt{3}\left(\left[\frac{Z-10}{Z-9}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-9)-\left(\frac{5}{24}-\frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}\right)} \\ = \frac{2}{\sqrt{3}\left(\frac{Z-10}{Z-9}\right)\left(\frac{5}{24}-\frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}}$$

 $r_3$  in units of  $a_0$ 

two indistinguishable spin-paired electrons in an orbitsphere with radius  $r_{12}$  given by:

$$r_{12} = \frac{a_0}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)^2} \pm a_0 \left(\frac{1}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}{20\sqrt{3}\left(\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)r_{10}\right)} - \frac{20\sqrt{3}\left(\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)r_{10}\right)}{2}\right)}{2}$$

 $r_{10}$  in units of  $a_0$ 

and n-12 electrons in a 3p orbitsphere with radius  $r_n$  given by

$$r_{n} = \frac{a_{0}}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)^{\pm} a_{0}} \left(\frac{1}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)^{2}} + \frac{20\sqrt{3}\left(\left[\frac{Z - n}{Z - (n-1)}\right]\left(1 - \frac{\sqrt{2}}{2} + \frac{1}{2}\right)r_{12}\right)}{\left((Z - (n-1)) - \left(\frac{A}{8} - \frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}\right)$$

 $r_{12}$  in units of  $a_0$ 

5 where the positive root must be taken in order that  $r_n > 0$ ;

the parameter A corresponds to the diamagnetic force,  $\mathbf{F}_{diamagnetic}$ :

$$\mathbf{F}_{diamagnetic} = -\sum_{m} \frac{\left(\ell + |m|\right)!}{\left(2\ell + 1\right)\left(\ell - |m|\right)!} \frac{\hbar^2}{4m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r, \text{ and the parameter } B \text{ corresponds to}$$

the paramagnetic force,  $\mathbf{F}_{mag 2}$ :

$$\mathbf{F}_{mog 2} = \frac{1}{Z} \frac{\hbar^2}{m_r r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

10 
$$\mathbf{F}_{mag 2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

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$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r, \text{ and}$$

$$\mathbf{F}_{mag 2} = \frac{1}{Z} \frac{8\hbar^2}{m_e r_n^2 r_{12}} \sqrt{s(s+1)} \mathbf{i}_r$$

5 wherein the parameters of thirteen to eighteen-electron atoms are

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Atom	Electron	Ground	908 Orbital	Diamagn	Paramag
Type	Configuration	State	Arrangement	etic	netic
Type	Comment.	Term	•	Force	Force
			3p Electrons	Factor	Factor
			(3p state)	A	В
Neutral 13 e Atom	$1s^2 2s^2 2p^6 3s^2 3p^1$	$^{2}P_{1/2}^{0}$	1 0 -1	11/3	0
Neutral 14 e Atom	$1s^2 2s^2 2p^6 3s^2 3p^2$	$^{3}P_{0}$	$\begin{array}{c c} \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array}$	7/3	0
Atom	$1s^2 2s^2 2p^6 3s^2 3p^3$	<sup>4</sup> S <sub>3/2</sub>	$\begin{array}{c c} \uparrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array}$	5 3	2
P Neutral 16 e Atom	$1s^2 2s^2 2p^6 3s^2 3p^4$	<sup>3</sup> P <sub>2</sub>	$\begin{array}{cccc} \uparrow & \uparrow & \uparrow \\ \hline 1 & 0 & -1 \end{array}$	4/3	1
S Neutral 17 e Atom Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$	$^{2}P_{3/2}^{0}$	$\begin{array}{cccc} \uparrow & \downarrow & \uparrow & \downarrow & \uparrow \\ \hline 1 & 0 & -1 & \end{array}$	2 3	2

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14 e Ion 
$$1s^2 2s^2 2p^6 3s^2 3p^2$$
  ${}^{3}P_0$   ${}^{\uparrow}$   ${}^{\uparrow}$   ${}^{\uparrow}$   ${}^{\downarrow}$   ${}^{1}$   ${}^{0}$   ${}^{-1}$   ${}^{1}$   ${}^{3}$  16

15 e Ion 
$$1s^2 2s^2 2p^6 3s^2 3p^3$$
  ${}^4S_{3/2}^0$   $\uparrow$   $\uparrow$   $\uparrow$   $\uparrow$   $\uparrow$   $\downarrow$  1 0 -1 0 24

16 e Ion 
$$1s^2 2s^2 2p^6 3s^2 3p^4$$
  $^3P_2$   $\xrightarrow{\uparrow}$   $\xrightarrow{\uparrow}$   $\xrightarrow{\uparrow}$   $\xrightarrow{1}$   $\xrightarrow{3}$  24

17 e Ion 
$$1s^2 2s^2 2p^6 3s^2 3p^5$$
  ${}^2P_{3/2}^0$   $\frac{\uparrow}{1}$   $\frac{\uparrow}{0}$   $\frac{\uparrow}{-1}$   $\frac{2}{3}$  32

18 e Ion 
$$1s^2 2s^2 2p^6 3s^2 3p^6$$
  ${}^{1}S_0$   $\xrightarrow{\uparrow} \xrightarrow{\downarrow} \xrightarrow{\uparrow} \xrightarrow{\downarrow}$  10 40

- 161. The system of claim 160 wherein the bond comprises a H<sub>2</sub>-type MO with two paired electron wherein the formation of the H<sub>2</sub>-type MO by the contribution of an electron from each participating atom results in a diamagnetic force between the remaining atomic electrons
  5 and the H<sub>2</sub>-type MO which causes the H<sub>2</sub>-type MO to move to greater principal axes than would result with the Coulombic force alone.
- 162. The system of claim 161 wherein the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining atomic
  10 electrons of each atom decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms.
- 163. The system of claim 162 wherein the general equation for the central Coulomb force on the outer-most shell (nth where n = Z 1) electron due to the nucleus and the inner 15 electrons is given by:

$$\mathbf{F}_{ele} = \frac{2e^2}{4\pi\varepsilon_0 r_n^2} \mathbf{i}_r$$

for  $r > r_{n-1}$ .

164. The system of claim 163 wherein the general equation for  $\mathbf{F}_{diamognetic}$  due to the p-orbital contribution is given by

5 
$$\mathbf{F}_{diamognetic} = -A \frac{\hbar^2}{12m_a r_n^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r$$

165. The system of claim 164 wherein the general equation for  $\mathbf{F}_{mag 2}$  is given by

$$\mathbf{F}_{mag 2} = B \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$

10 166. The system of claim 165 wherein the general equation for  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is given by

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{1}{2}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_s \hbar^2}{m_e r_n^4} 10\sqrt{s(s+1)} \mathbf{i_r}$$

167. The system of claim 166 wherein the general equation for  $\mathbf{F}_{mag 3}$ , due to the contribution of a 2p electron from each binding atom in the formation of the  $\sigma$  MO that

gives rise to a paramagnetic force on the remaining two 2p electrons that pair, is given by

$$\mathbf{F}_{mag 3} = C \frac{\hbar^2}{4m_e r_n^3} \sqrt{s(s+1)} \mathbf{i}_r$$

- 168. The system of claim 167 wherein the parameters A, B, and C are zero or a positive20 integer such that the resulting energy of the molecule is minimized and the electron angular momentum is conserved in the formation of the specie.
- 169. The system of claim 168 wherein the radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic and paramagnetic25 forces:

10

$$\frac{m_e v_n^2}{r_n} = \begin{pmatrix} \frac{2e^2}{4\pi\varepsilon_0 r_n^2} - A\frac{\hbar^2}{12m_e r_n^2 r_3} \sqrt{s(s+1)} + B\frac{\hbar^2}{Zm_e r_n^2 r_3} \sqrt{s(s+1)} \\ -\left[\frac{1}{2}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r^4 m} 10\sqrt{s(s+1)} + C\frac{\hbar^2}{4m r^3} \sqrt{s(s+1)} \end{pmatrix}$$

- 170. The system of claim 169 wherein the radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic and paramagnetic
- 5 forces where the velocity given by  $v_n = \frac{\hbar}{m_e r_n}$  and  $s = \frac{1}{2}$  gives:

$$\frac{\hbar^2}{m_e r_n^3} - C \frac{\hbar^2}{4 m_e r_n^3} \sqrt{\frac{3}{4}} = \frac{2e^2}{4 \pi \varepsilon_0 r_n^2} - A \frac{\hbar^2}{12 m_e r_n^2 r_3} \sqrt{\frac{3}{4}} + B \frac{\hbar^2}{Z m_e r_6^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{1}{2}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_n^4 m_e} 10 \sqrt{\frac{3}{4}}$$

171. The system of claim 170 wherein the general equation for the radius of the shell of the remaining electrons is given by

$$r_{6} = \frac{a_{0}\left(1 - C\frac{\sqrt{3}}{8}\right)}{\left(2 - \left(\frac{A}{12} - \frac{B}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{\frac{1}{2}}} \pm a_{0} \left(\frac{1 - C\frac{\sqrt{3}}{8}}{\left(2 - \left(\frac{A}{12} - \frac{B}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{2}}{\left(2 - \left(\frac{A}{12} - \frac{B}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}\right)$$

 $r_{a}$  in units of  $a_{0}$ 

172. The system of claim 171 wherein the radii  $r_3$  are given by

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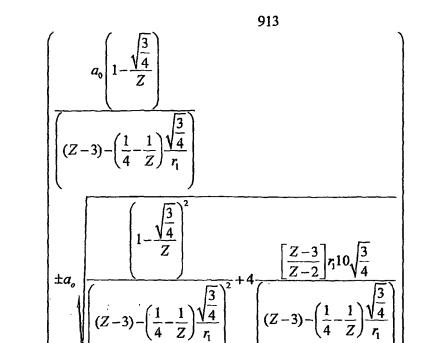
$$r_{4} = r_{3} = \frac{\left(z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}}{\left(z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}} - \frac{\left[\frac{z - 3}{z - 2}\right] r_{1} 10 \sqrt{\frac{3}{4}}}{\left(z - 3\right) - \left(\frac{1}{4} - \frac{1}{z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}}\right)}{2}$$

 $r_1$  in units of  $a_o$ 

- 173. The system of claim 172, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration  $1s^22s^22p^{n-4}$ , there are two
- 5 indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by:

$$r_1 = r_2 = a_o \left[ \frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right]$$

and two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by:



r, in units of a

174. The system of claim 173 wherein the sum  $E_r$  (molecule, AOs) of the Coulombic energy change of the AO electrons of both atoms of a bond is given by using the initial radius  $r_n$  of each atom and the final radius  $r_{n-1}$  of the binding shell of each atom and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell:

$$E_{T}(molecule, AOs) = \sum_{m=n_{1}-3}^{n_{1}-2} \frac{(Z-m)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{n_{1}-1}} - \frac{1}{r_{n_{1}}}\right) + \sum_{m=n_{2}-3}^{n_{2}-2} \frac{(Z-m)e^{2}}{8\pi\varepsilon_{0}} \left(\frac{1}{r_{n_{2}-1}} - \frac{1}{r_{n_{2}}}\right)$$

where the subscript designates atom 1 and atom 2 of the bond.

10

175. The system of claim 174 wherein the forces on the electrons of the MO are the Coulombic force:

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_{\xi};$$

the spin pairing force:

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$

the diamagnetic force:

$$\mathbf{F}_{diamagneticMO1} = -\frac{n_e \hbar^2}{4m_e a^2 b^2} D\mathbf{i}_{\xi}$$

where  $n_e$  is the total number of electrons that interact with the binding  $\sigma$ -MO electron, the 5 force on the pairing electron of the  $\sigma$  MO:

$$\mathbf{F}_{diamagneticMO2} = -\frac{1}{Z} \frac{|L|\hbar}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$

where |L| is the magnitude of the angular momentum of each atom at a focus that is the source of the diamagnetism at the  $\sigma$ -MO, and the centrifugal force:

 $\mathbf{F}_{centrifugallMO} = -\frac{\hbar^2}{m_e a^2 b^2} Di_{\xi}$ , wherein the force balance of the centrifugal force equated

10 to the Coulombic and magnetic forces is solved for the length of the semimajor axis.

176. The system of claim 175 wherein the force balance equation for the  $\sigma$ -MO with  $n_e = 2$  and  $|L| = \hbar$  is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\epsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$

$$15 a = \left(2 + \frac{1}{Z}\right) a_0$$

177. The system of claim 176 wherein the force balance equation for the  $\sigma$ -MO with

$$n_e = 2$$
 and  $|L| = \sqrt{\frac{3}{4}}\hbar$  is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi \varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(\frac{3}{2} + \frac{\sqrt{\frac{3}{4}}}{Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$

$$20 a = \left(\frac{5}{2} + \frac{\sqrt{\frac{3}{4}}}{Z}\right) a_0$$

178. The system of claim 177 wherein the force balance equation for the  $\sigma$ -MO  $n_e=2$ , and  $|L|=\hbar$ :

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(\frac{5}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$

$$a = \left(\frac{7}{2} + \frac{1}{2Z}\right) a_0$$

179. The system of claim 178 wherein the Coulombic force is

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_{\xi};$$

the spin pairing force is

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D \mathbf{i}_{\xi}$$

the force on the electrons of the MO due to two paired electrons in at least one shell with  $n_e = 2$  is

$$\mathbf{F}_{dlamagneticMO1} = -\frac{\hbar^2}{2m_a^2b^2}D\mathbf{i}_{\xi};$$

the force  $\mathbf{F}_{diamagneticMO2}$  is given by the sum of the contributions over the components of angular momentum |L| of the atoms at the foci acting on the electrons of the  $\sigma$ -MO:

$$\mathbf{F}_{diamagneticMO2} = -\sum_{i,j} \frac{|L_i|\hbar}{Z_j 2m_e \alpha^2 b^2} D\mathbf{i}_{\xi}$$
, and

the centrifugal force is

$$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_{\xi}.$$

20 180. The system of claim 179 wherein the force balance equation for the  $\sigma$ -MO of the carbon nitride radical comprising carbon with charge  $Z_1=6$  and  $|L_1|=\hbar$  and  $|L_2|=\sqrt{\frac{3}{4}}\hbar$  and nitrogen with  $Z_2=7$  and  $|L_3|=\hbar$  is

$$\frac{\hbar^{2}}{m_{e}a^{2}b^{2}}D = \frac{e^{2}}{8\pi\varepsilon_{0}ab^{2}}D + \frac{\hbar^{2}}{2m_{e}a^{2}b^{2}}D - \left(1 + \frac{1}{Z_{1}} + \frac{\sqrt{\frac{3}{4}}}{Z_{1}} + \frac{1}{Z_{2}}\right)\frac{\hbar^{2}}{2m_{e}a^{2}b^{2}}D$$

$$a = \left(2 + \frac{1}{Z_{1}} + \frac{\sqrt{\frac{3}{4}}}{Z_{1}} + \frac{1}{Z_{2}}\right)a_{0}$$

181. The system of claim 180 wherein the Coulombic force is

5 
$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_{\xi};$$

the spin pairing force is

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$

the force on the electrons of the MO due to two paired electrons in at least one shell with  $n_{e_1} = 2$  is

$$\mathbf{F}_{diamagneticMO1} = -\frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi};$$

the force  $\mathbf{F}_{diamogneticMO2}$  is given by the sum of the contributions over the components of angular momentum |L| of the atoms at the foci acting on the electrons of the  $\sigma$ -MO:

$$\mathbf{F}_{diamagneticMO2} = -\sum_{i,j} \frac{|L_i|\hbar}{Z_i 2m_e a^2 b^2} D\mathbf{i}_{\xi}$$
, and

the centrifugal force is

15 
$$\mathbf{F}_{centrifugalIMO} = -\frac{\hbar^2}{m_{c}a^2b^2}D\mathbf{i}_{\xi}.$$

182. The system of claim 181 wherein the force balance equation for the  $\sigma$ -MO of the carbon nitride radical comprising carbon with charge  $Z_1=6$  and  $|L_1|=\hbar$  and  $|L_2|=\sqrt{\frac{3}{4}}\hbar$  and nitrogen with  $Z_2=7$  and  $|L_3|=\hbar$  is

$$\frac{\hbar^{2}}{m_{e}a^{2}b^{2}}D = \frac{e^{2}}{8\pi\varepsilon_{0}ab^{2}}D + \frac{\hbar^{2}}{2m_{e}a^{2}b^{2}}D - \left(1 + \frac{1}{Z_{1}} + \frac{\sqrt{\frac{3}{4}}}{Z_{1}} + \frac{1}{Z_{2}}\right)\frac{\hbar^{2}}{2m_{e}a^{2}b^{2}}D$$

$$a = \left(2 + \frac{1}{Z_{1}} + \frac{\sqrt{\frac{3}{4}}}{Z_{1}} + \frac{1}{Z_{2}}\right)a_{0}$$

183. The system of claim 182 wherein the Coulombic force is

5 
$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_{\xi};$$

the spin pairing force is

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$

the force on the electrons of the MO due to two paired electrons in at least one shell with  $n_s = 2$  is

$$\mathbf{F}_{diamagneticMO1} = -\frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi};$$

the force  $\mathbf{F}_{diamagneticMO2}$  is given by the sum of the contributions over the components of angular momentum |L| of the atoms at the foci acting on the electrons of the  $\sigma$ -MO, and the sum of the contributions from atom 1 with  $Z=Z_1$  and atom 2 with  $|L_1|=\hbar$  is

$$\mathbf{F}_{diamagneticMO2} = -\left(\frac{1}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}, \text{ and }$$

15 the centrifugal force is

$$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_{\xi}.$$

184. The system of claim 183 wherein force balance equation for the  $\sigma$ -MO of the carbon monoxide molecule is

$$20 \qquad \frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \left(\frac{1}{Z_1} + \frac{1}{Z_2}\right)\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$

$$a = \left(2 + \frac{1}{Z_1} + \frac{1}{Z_2}\right) a_0$$

185. The system of claim 184 wherein the Coulombic force is

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_{\xi};$$

5 the spin pairing force is

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$

the force on the electrons of the MO due to two paired electrons in at least one shell with  $n_a = 2$  is

$$\mathbf{F}_{diamagneticMO1} = -\frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi};$$

10 the force  $\mathbf{F}_{diamagneticMO2}$  of the nitric oxide radical comprising nitrogen with charge  $Z_1=7$  and  $|L_1|=\hbar$  and  $|L_2|=\sqrt{\frac{3}{4}}\hbar$  and oxygen with  $Z_2=8$  and  $|L_3|=\hbar$  given by the corresponding sum of the contributions is

$$\mathbf{F}_{diamagneticMO2} = -\left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}, \text{ and}$$

the centrifugal force is

15 
$$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_{\xi}.$$

186. The system of claim 185 wherein the general force balance equation for the  $\sigma$ -MO of the nitric oxide radical is the same as that of CN:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$

$$a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) a_0$$

where  $Z_1 = 7$  and  $Z_2 = 8$  for NO and  $Z_1 = 6$  and  $Z_2 = 7$  for CN.

- 187. The system of claims 186 and 63 wherein the distance from the origin of the H<sub>2</sub>-type5 ellipsoidal-MO to each focus c', the internuclear distance 2c', and the length of the semiminor axis of the prolate spheroidal H<sub>2</sub>-type MO b = c are solved from the semimajor axis a.
- 188. The system of claim 187 wherein the potential energy of the two electrons in the 10 central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi \varepsilon_a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}};$$

The potential energy of the two nuclei is

$$V_p = n_1 \frac{e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}};$$

The kinetic energy of the electrons is

15 
$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}, \text{ and}$$

The energy,  $V_m$ , of the magnetic force between the electrons is

$$V_m = n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
, and

the total energy,  $E_T$ , is given by the sum of the energy terms plus E(AO):

$$E_T = V_e + T + V_m + V_p$$

$$E_{T} = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right]$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right]$$

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where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and E(AO) is the energy of the at least one atomic orbital to which the 5 MO is energy matched.

189. The system of claim 188 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

10 
$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}$$
, and

the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc} .$$

190. The system of claim 189 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1 \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}, \text{ and}$$

the total energy is

$$E_T = V_e + T + V_m + V_n + \overline{E}_{osc}$$

$$20 \quad E_{T} = -\left\{ -\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_{1}c_{2}e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - n_{1}\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right]$$

where R is b or a,  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and E(AO) is the energy of the at least one atomic orbital to which the MO is energy matched.

- 191. The system of claim 190 wherein the bond comprises a H<sub>2</sub>-type MO with four paired electron wherein the formation of the H<sub>2</sub>-type MO by the contribution of two electrons from each participating atom results in a diamagnetic force between the remaining atomic electrons and the H<sub>2</sub>-type MO which causes the H<sub>2</sub>-type MO to move to greater principal axes than 5 would result with the Coulombic force alone.
- 192. The system of claim 191 wherein the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining atomic electrons of each atom decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms.
  - 193. The system of claim 192 wherein the general equation for the central Coulomb force on the outer-most shell (nth where n = Z 2) electron due to the nucleus and the inner electrons is given by:

$$\mathbf{F}_{ele} = \frac{3e^2}{4\pi\varepsilon_0 r_n^2} \mathbf{i_r}$$

for  $r > r_{n-1}$ .

194. The system of claim 193 wherein the general equation for  $\mathbf{F}_{diamagnetic}$  due to the p-orbital contribution is given by

$$\mathbf{F}_{diamagnetic} = -A \frac{\hbar^2}{12m_e r_n^2 r_3} \sqrt{\frac{3}{4}} \mathbf{i}_r$$

195. The system of claim 194 wherein the general equation for  $\mathbf{F}_{mag 2}$  is given by

$$\mathbf{F}_{mag 2} = B \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)} \mathbf{i}_r$$

25

196. The system of claim 195 wherein the general equation for  $\mathbf{F}_{diamagnetic\ 2}$  due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is given by

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{2}{3}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{m.r_s^4} 10\sqrt{s(s+1)} \mathbf{i}_r$$

197. The system of claim 196 wherein the general equation for F<sub>mag 3</sub>, due to the contribution of a 2p electron from each binding atom in the formation of the σ MO that
5 gives rise to a paramagnetic force on the remaining two 2p electrons that pair, is given by

$$\mathbf{F}_{mag \ 3} = C \frac{\hbar^2}{4m_e r_n^3} \sqrt{s(s+1)} \mathbf{i}_r$$

- 198. The system of claim 197 wherein the parameters A, B, and C are zero or a positive integer such that the resulting energy of the molecule is minimized and the electron angular momentum is conserved in the formation of the specie.
  - 199. The system of claim 198 wherein the radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic and paramagnetic forces:

15 
$$\frac{m_e v_n^2}{r_n} = \begin{pmatrix} \frac{3e^2}{4\pi\varepsilon_0 r_n^2} - A\frac{\hbar^2}{12m_e r_n^2 r_3} \sqrt{s(s+1)} + B\frac{\hbar^2}{Zm_e r_n^2 r_3} \sqrt{s(s+1)} \\ -\left[\frac{2}{3}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_n^4 m_e} 10\sqrt{s(s+1)} + C\frac{\hbar^2}{4m_e r_n^3} \sqrt{s(s+1)} \end{pmatrix}$$
 (13.626)

200. The system of claim 199 wherein the radius of the 2p shell is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic and paramagnetic forces where the velocity given by  $v_n = \frac{\hbar}{m_e r_n}$  and  $s = \frac{1}{2}$  gives:

$$20 \quad \frac{\hbar^2}{m_e r_n^3} - C \frac{\hbar^2}{4m_e r_n^3} \sqrt{\frac{3}{4}} = \frac{3e^2}{4\pi\varepsilon_0 r_n^2} - A \frac{\hbar^2}{12m_e r_n^2 r_3} \sqrt{\frac{3}{4}} + B \frac{\hbar^2}{Zm_e r_0^2 r_3} \sqrt{\frac{3}{4}} - \left[\frac{2}{3}\right] \left(1 - \frac{\sqrt{2}}{2}\right) \frac{r_3 \hbar^2}{r_n^4 m_e} 10\sqrt{\frac{3}{4}}$$

201. The system of claim 200 wherein the general equation for the radius of the shell of the remaining electrons is given by

$$r_{6} = \frac{a_{0}\left(1 - C\frac{\sqrt{3}}{8}\right)}{\left(3 - \left(\frac{A}{12} - \frac{B}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)^{\pm} a_{0}} + \frac{20\sqrt{3}\left(\left[\frac{2}{3}\right]\left(1 - \frac{\sqrt{2}}{2}\right)r_{3}\right)}{\left(3 - \left(\frac{A}{12} - \frac{B}{Z}\right)\frac{\sqrt{3}}{2r_{3}}\right)}$$

 $r_3$  in units of  $a_0$ 

202. The system of claim 201 wherein the radii  $r_3$  are given by

$$r_{4} = r_{3} = \frac{\left(2 - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}}{\left(2 - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}} + \frac{\left[\frac{Z - 3}{Z - 2}\right] r_{1} 10 \sqrt{\frac{3}{4}}}{\left(Z - 3\right) - \left(\frac{1}{4} - \frac{1}{Z}\right) \frac{\sqrt{\frac{3}{4}}}{r_{1}}}\right)}{2}$$

 $r_1$  in units of  $a_0$ 

5

203. The system of claim 202, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration  $1s^22s^22p^{n-4}$ , there are two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_1$  and  $r_2$  both given by:

$$r_1 = r_2 = a_o \left[ \frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right];$$

and two indistinguishable spin-paired electrons in an orbitsphere with radii  $r_3$  and  $r_4$  both given by:

$$r_{4} = r_{3} = \frac{\left(\frac{\sqrt{\frac{3}{4}}}{2}\right)}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)} \left(\frac{\left(\frac{1-\sqrt{\frac{3}{4}}}{Z}\right)^{2}}{\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)^{2} + 4\left(\frac{Z-3}{Z-2}\right)r_{1}10\sqrt{\frac{3}{4}}}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)^{2} + 4\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_{1}}\right)^{2}}\right)$$

 $r_1$  in units of  $a_o$ 

5

204. The system of claim 203 wherein the force balance of a double-bond MO corresponds to that of a second pair of two electrons binding to a molecular ion having +2e at each focus and a first bound pair such that the forces are the same as those of a molecule ion having +e at each focus.

10

205. The system of claim 204 wherein the forces on the electrons of the MO are the Coulombic force:

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_{\xi};$$

the spin pairing force:

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi};$$

the diamagnetic force:

$$\mathbf{F}_{diamogneticMO1} = -\frac{n_e \hbar^2}{4m_e a^2 b^2} D\mathbf{i}_{\xi}$$

where  $n_e$  is the total number of electrons that interact with the binding  $\sigma$ -MO electron;

5 the force on the pairing electron of the  $\sigma$  MO:

$$\mathbf{F}_{diamagneticMO2} = -\frac{1}{Z} \frac{|L|\hbar}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$

where |L| is the magnitude of the angular momentum of each atom at a focus that is the source of the diamagnetism at the  $\sigma$ -MO, and

the centrifugal force:

10 
$$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_{\xi}, \text{ and}$$

the force balance of the centrifugal force equated to the Coulombic and magnetic forces is solved for the length of the semimajor axis.

206. The system of claim 205 wherein the forces on the electrons of the  $NO_2$  MO are the 15 Coulombic force:

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_{\xi};$$

the spin pairing force:

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_{.}a^2b^2}D\mathbf{i}_{\xi};$$

the diamagnetic force  $\mathbf{F}_{diamagneticMO1}$  for each  $\sigma$ -MO of the  $NO_2$  molecule due to the 20 two paired electrons in the O2p shell with  $n_e = 2$ :

$$\mathbf{F}_{diamogneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$

which is also the corresponding force of NO;

 $\mathbf{F}_{diamagneticMO2}$  of the nitrogen dioxide molecule comprising nitrogen with charge  $Z_1 = 7$ 

and  $|L_1| = \hbar$  and  $|L_2| = \sqrt{\frac{3}{4}}\hbar$  and the two oxygen atoms, each with  $Z_2 = 8$  and  $|L_3| = \hbar$  given by the corresponding sum of the contributions:

$$\mathbf{F}_{diamagneticMO2} = \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_{\xi}$$

which is also the corresponding force of NO and CN except the term due to oxygen is twice 5 that of NO due to the two oxygen atoms of  $NO_2$ , and

the centrifugal force

$$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_{\xi}$$
, and

the force balance of the centrifugal force equated to the Coulombic and magnetic forces is solved for the length of the semimajor axis.

10

207. The system of claim 206 wherein the force balance equation for the  $\sigma$ -MOs of  $NO_2$  with  $Z_1 = 7$  and  $Z_2 = 8$  is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$

15  $a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) a_0$ 

208. The system of claims 207 and 63 wherein the distance from the origin of the  $H_2$ -type-ellipsoidal-MO to each focus c', the internuclear distance 2c', and the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO b=c are solved from the semimajor 20 axis a.

- 209. The system of claim 208 wherein the sum  $E_T$  (molecule, AOs) of the Coulombic energy change of the AO electrons of the participating atoms or ions of the bonds of the specie is the sum of the contributions over all such atoms or ions given by using the initial radius  $r_n$  of the atom or ion and the final radius  $r_{n-2}$  of the binding shell of the atom or ion
- 5 and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell:

$$E_T(molecule, AOs) = \sum_{m=n_1-4}^{n_1-3} \frac{(Z-m)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_{n_1-2}} - \frac{1}{r_{n_1}}\right)$$

where the subscript designates the exemplary atom 1 of the bond.

- 10 210. The system of claim 209 wherein the sum  $E_T$  (molecule, AOs) of the Coulombic energy change of the AO electron of a participating atom of a bond wherein all of the electrons of the shell of the AO are contributed to the bond is given by the sum of the corresponding ionization energies of the AO electrons.
- 15 211. The system of claim 210 wherein energy of the double bond MO is match to the participating AOs and the potential energy of the four electrons in the central field of the nuclei at the foci is

$$V_e = 2^2 n_1 c_1 c_2 \frac{-2e^2}{8\pi\epsilon \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}};$$

The potential energy of the two nuclei is

20 
$$V_p = 2^2 n_1 \frac{e^2}{8\pi\varepsilon_0 \sqrt{a^2 - b^2}};$$

The kinetic energy of the electrons is

$$T = 2n_1c_1c_2\frac{\hbar^2}{2m_1a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}$$
, and

The energy,  $V_m$ , of the magnetic force between the electrons is

$$V_m = 2^2 n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
, and

25 The total energy,  $E_T$ , is given by the sum of the energy terms plus E(AO):

$$E_{T} = V_{e} + T + V_{m} + V_{p}$$

$$E_{T} = -\frac{2^{2} n_{l} e^{2}}{8\pi\varepsilon_{o} \sqrt{a^{2} - b^{2}}} \left[ c_{1}c_{2}(2) \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right] + n_{l}E(AO)$$

$$= -\frac{2^{2} n_{l} e^{2}}{8\pi\varepsilon_{o}c'} \left[ c_{1}c_{2}(2) \ln \frac{a + c'}{a - c'} - 1 \right] + n_{l}E(AO)$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and E(AO) is the energy of the at least one atomic orbital to which the MO is energy matched.

212. The system of claim 211 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}$$
, and

the total energy is

$$E_T = V_e + T + V_m + V_p + E(AO) + \overline{E}_{osc}.$$

15

213. The system of claim 212 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

$$E_T = -2^2 \frac{n_1 e^2}{8\pi\varepsilon_0 c'} \left[ c_1 c_2 \left( 2 \right) \ln \frac{a + c'}{a - c'} - 1 \right] + n_1 E \left( AO \right) + \overline{E}_{osc}$$

20 where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and E(AO) is the energy of the at least one atomic orbital to which the MO is energy matched.

- 214. The system of claim 213 wherein the energy components of are  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$ , except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to each  $\sigma$ -MO double bond.
- 5 215. The system of claim 214 wherein the potential energy of the four electrons of double bond in the central field of the nuclei at the foci is

$$V_{e} = 2^{2} n_{1} c_{1} c_{2} \frac{-2e^{2}}{8\pi\varepsilon_{o} \sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}};$$

The potential energy of the two nuclei is

$$V_p = 2^2 n_1 \frac{e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}};$$

10 The kinetic energy of the electrons is

$$T = 2n_1c_1c_2 \frac{\hbar^2}{2m_2a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
, and

The energy,  $V_m$ , of the magnetic force between the electrons is

$$V_m = 2^2 n_1 c_1 c_2 \frac{-\hbar^2}{4m \cdot a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
, and

The total energy,  $E_T$ , is given by the sum of the energy terms:

$$E_T = V_e + T + V_m + V_p$$

$$E_{T} = -\frac{2^{2} n_{1} e^{2}}{8\pi\varepsilon_{o} \sqrt{a^{2} - b^{2}}} \left[ c_{1} c_{2}(2) \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right]$$
$$= -\frac{2^{2} n_{1} e^{2}}{8\pi\varepsilon_{o} c'} \left[ c_{1} c_{2}(2) \ln \frac{a + c'}{a - c'} - 1 \right]$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie, and  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic 20 orbitals of each chemical bond.

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216. The system of claim 215 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{asc} = \overline{E}_D + \overline{E}_{Kvib}$$
 , and

5 the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}.$$

217. The system of claim 216 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is 10 the difference between the Doppler and average vibrational kinetic energies:

$$E_{T} = -\frac{2^{2} n_{1} e^{2}}{8\pi \varepsilon_{0} c'} \left[ c_{1} c_{2} \left( 2 \right) \ln \frac{a + c'}{a - c'} - 1 \right] + \overline{E}_{osc}$$

 $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie, and  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

- 218. The system of claim 217 wherein the total energy of the specie is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms, the change in the energy of the AOs or HOs upon forming the bond, the change in magnetic energy with bond formation, and the energy of oscillation in the transition state.
- 219. The system of claim 218 wherein the total energy of the specie is the sum over all of the component groups wherein the total energy of each said group is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms, the change in the energy of the AOs or HOs upon forming the bond, the change in magnetic energy with bond formation, and the energy of oscillation in the transition state.
- 30 220. The system of claim 219 wherein the change in magnetic energy is given by

$$E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_n^3} = \frac{8\pi\mu_o \mu_B^2}{r_n^3}$$

where  $r_n^3$  is the radius of the atom that reacts to form the bond.

- 221. The system of claim 220 wherein the bond energy of the molecular or molecular ion5 is difference in the energy of the total energy of the starting species and the total energy of the specie.
- 222. The system of claim 221 wherein the bond energy of a specific bond of the molecular or molecular ion is difference in the energy of the sum of the energies of the atoms and any change in energy of any groups formed with the starting atoms and the total energy of the bond of the specie.
  - 223. The system of claim 222 wherein the total energy of a molecule,  $E_T$  (molecule), is given by the sum of:
- the sum of the energies of the electrons donated to each bond,

the sum of the energies of electrons of at least one other atom donated to the bonds,

the sum over the participating atoms of each AO contribution due to the decrease in radius with the formation of each bond, and

the  $\sigma$  MO energy contribution per bond.

20

224. The system of claim 223 wherein the total energy of a molecule,  $E_T$  (molecule), is given by the sum of:

the sum of the energies of the electrons donated to each bond such that all of the electrons of the shell are donated,

25 the sum of the energies of electrons of at least one other atom donated to the bonds, the sum over the participating atoms of each AO contribution due to the decrease in radius with the formation of each bond, and

the  $\sigma$  MO energy contribution per bond.

225. The system of claim 223 wherein the total energy of  $CO_2$ ,  $E_T(CO_2)$ , is given by the sum of E(ionization; C) and  $E(ionization; C^+)$ , the sum of the energies of the first and second electrons of carbon donated to each double bond, the sum of E(ionization; O) and two times  $E(ionization; O^+)$ , the energies of the first and second electrons of oxygen donated to the double bonds, two times  $E_T(O,2p)$ , the O2p AO contribution due to the decrease in radius with the formation of each bond and two times  $E_T(C=O,\sigma)$ , the  $\sigma$  MO contribution:

$$\begin{split} E_T(CO_2) = &\begin{pmatrix} E(ionization;\ C) + E(ionization;\ C^+) + E(ionization;\ O) \\ + 2E(ionization;\ O^+) + 2E_T(O,2p) + 2E_T(C=O,\sigma) \end{pmatrix} \\ = &\begin{pmatrix} 11.26030\ eV + 24.38332\ eV + 13.61806\ eV \\ + 2(35.11730\ eV) + 2(-32.12759\ eV) \\ -2 \begin{pmatrix} \frac{4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}} \begin{pmatrix} \left(\frac{3}{2}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}} - 1 \\ a-\sqrt{\frac{2aa_0}{3}} \end{pmatrix} \end{pmatrix} \\ = &\begin{pmatrix} 11.26030\ eV + 24.38332\ eV + 13.61806\ eV \\ + 2(35.11730\ eV) + 2(-32.12759\ eV) - 2(55.25423\ eV) \end{pmatrix} \\ = -55.26841\ eV \end{split}$$

10

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

- 15 226. The system of claim 225 wherein the total energy of a molecule,  $E_{T+osc}$  (molecule) is given by the sum of  $E_T$  (molecule) and  $\overline{E}_{osc}$ .
- 227. The system of claim 226 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is 20 the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = n_1 \left( \overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left( E_{hv} \sqrt{\frac{2\overline{E}_K}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right), \text{ and}$$

where the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{c_{BO} \frac{c_1 c_2 e^2}{4\pi \varepsilon_0 R^3}}{m_e}};$$

the kinetic energy,  $E_{\scriptscriptstyle K}$ , is given by Planck's:

5 
$$\overline{E}_{K} = \hbar \omega = \hbar \sqrt{\frac{c_{BO} \frac{c_{1}c_{2}e^{2}}{4\pi\varepsilon_{0}R^{3}}}{m_{e}}};$$

15

the Doppler energy of the electrons of the reentrant orbit is

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{m_e c^2}} = E_{h\nu} \sqrt{\frac{2\hbar \sqrt{\frac{c_{BO} \frac{c_1 c_2 e^2}{4\pi \varepsilon_0 R^3}}{m_e}}}{\frac{m_e}{m_e c^2}}}$$

 $\overline{E}_{osc}$  is given by the sum of and  $\overline{E}_{Kvib}$ , the vibrational energy:

$$\overline{E}_{osc}(molecule) = n_1(\overline{E}_D + \overline{E}_{Kvib}) = n_1\left(E_{hv}\sqrt{\frac{\frac{c_1c_2e^2}{4\pi\varepsilon_0R^3}}{\frac{m_e}{m_ec^2}} + E_{vib}}\right)$$

- 10 where R is b or a,  $n_1$  is the number of equivalent bonds of the MO,  $c_{BO}$  is the bond-order factor which is 1 for a single bond, 4 for a double bond, and 9 for a triplet bond,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie, and  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.
  - 228. The system of claim 227 wherein  $E_{h\nu}$  is given by  $E_{T}$  (molecule)/2 in the case of a double bond such that

$$\overline{E}_{osc} = \overline{E}_{D} + \overline{E}_{Kvib} = E_{T} \left( molecule \right) / 2 \sqrt{\frac{2\overline{E}_{K}}{Mc^{2}}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} .$$

229. The system of claim 228 wherein  $E_{hv}$  of a molecule having  $n_1$  bonds is given by  $E_T(molecule)/n_1$  such that

5 
$$\overline{E}_{osc} = n_1 \left( \overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left( E_T \left( molecule \right) / n_1 \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right).$$

230. The system of claim 229 wherein  $E_{hr}$  of a molecule having  $n_1$  bonds is given by  $E_T(H_2)$  such that

10 
$$\overline{E}_{asc} = n_1 \left( \overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left( E_T \left( H_2 \right) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right).$$

where  $E_T(H_2) = -31.63537 \ eV$  is the total energy of the hydrogen molecule, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm 10\%$ , if desired.

15 231. The system of claim 230 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = n_1 \left( \overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left( E_{hv} \sqrt{\frac{2\overline{E}_K}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right), \text{ and}$$

where the angular frequency of the reentrant oscillation in the transition state is determined 20 by the force between the central field and the electrons in the transition state; said force and its derivative are given by

$$f(R) = -c_{BO} \frac{c_1 c_2 e^2}{4\pi \varepsilon_0 R^3}$$

and

$$f'(a) = 2c_{BO} \frac{c_1 c_2 e^2}{4\pi \varepsilon_0 R^3}$$

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_1c_2e^2}{4\pi\epsilon_0R^3}}{m_e}}$$

where R is b or a,  $c_{BO}$  is the bond-order factor which is 1 for a single bond, 4 for a double bond, and 9 for a triplet bond,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie, and  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

- 232. The system of claim 231 wherein the nucleus of the B atom and the nucleus of the A atom comprise the foci of each  $H_2$ -type ellipsoidal MO of the A-B bond and the
- 10 parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the A-atom AO are determined from the polar equation of the ellipse:

$$r = r_0 \frac{1+e}{1+e\cos\theta'}$$

233. The system of claim 232 wherein the radius of the A shell is  $r_A$ , and the polar radial coordinate of the ellipse and the radius of the A shell are equal at the point of intersection such that

$$r_A = (a-c')\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\theta'}$$
, and

the polar angle  $\theta$ ' at the intersection point is given by

$$\theta' = \cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\frac{c'}{a}}{a_0}-1\right)\right)$$

20

234. The system of claim 233 wherein the angle  $\theta_{AAO}$  the radial vector of the A AO makes with the internuclear axis is

$$\theta_{AAO} = 180^{\circ} - \theta'$$

235. The system of claim 234 wherein the distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals such that the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the A radial vector obeys the following relationship:

$$5 r_A \sin \theta_{AAO} = b \sin \theta_{H_2MO}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{r_a \sin \theta_{AAO}}{b};$$

the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H,MO} = a \cos \theta_{H,MO}, \text{ and}$$

the distance  $d_{AAO}$  along the internuclear axis from the origin of the A atom to the point of intersection of the orbitals is given by

$$d_{AAO} = c' - d_{H_2MO}.$$

- 15 236. The system of claim 235 where the bond angle is determined from the zero energy condition of the total energy of the potential bond between any pair of terminal atoms.
  - 237. The system of claim 236 where the force constant k' of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{c_1 c_2 2e^2}{4\pi\varepsilon_0}$$

where  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie and  $c_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond.

25 238. The system of claim 237 where the distance from the origin of the MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi \varepsilon_0}{m_e e^2 2k' a}} = \sqrt{\frac{aa_0}{2k'}};$$

the internuclear distance is

$$2c'=2\sqrt{\frac{aa_0}{2k'}};$$

the length of the semiminor axis of the prolate spheroidal MO b = c is given by

$$b = \sqrt{a^2 - {c'}^2}$$
, and

and, the eccentricity, e, is

5 
$$e = \frac{c'}{a}$$

239. The system of claim 238 wherein the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}};$$

10 The potential energy of the two nuclei is

$$V_p = \frac{e^2}{8\pi\varepsilon_a \sqrt{a^2 - b^2}};$$

The kinetic energy of the electrons is

$$T = c_1 c_2 \frac{\hbar^2}{2m a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
, and

The energy,  $V_m$ , of the magnetic force between the electrons is

15 
$$V_m = c_1 c_2 \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}, \text{ and}$$

The total energy,  $E_T$ , is given by the sum of the energy terms:

$$E_T = V_e + T + V_m + V_p$$

$$\begin{split} E_T &= -\frac{e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right] \\ &= -\frac{e^2}{8\pi\varepsilon_0 c'} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \end{split}$$

where  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of

20 the specie, and  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

240. The system of claim 239 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_o + T + V_m + V_p\right) \sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1 \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}}, \text{ and}$$

5 The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_{T} = -\left\{ \frac{e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \left[ 1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_{1}c_{2}e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\}$$

where  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie, and  $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

241. The system of claim 240 wherein the vibrational energy  $\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$  is given by

$$+\frac{1}{2}\hbar\sqrt{\frac{c_1e^2}{8\pi\varepsilon_oa^3}-\frac{e^2}{8\pi\varepsilon_o(a+c')^3}}$$

where  $\mu$  is the reduced mass of the nuclei.

15

- 242. The system of claim 241 wherein the energy components of are  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$ , except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to a  $\sigma$ -MO double bond.
- 20 243. The system of claim 242 wherein  $c' = a \sqrt{\frac{\hbar^2 4\pi \varepsilon_0}{m_e e^2 2k'a}} = \sqrt{\frac{aa_0}{2k'}}$  is substituted into the equation for  $E_T$  which is set equal to zero, and the semimajor axis is solved.

244. The system of claims 243 and 63 wherein the distance from the origin of the  $H_2$ -type-ellipsoidal-MO to each focus c', the internuclear distance 2c', and the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO b=c are solved from the semimajor axis a.

5

245. The system of claim 244 wherein with  $2c'_{A-B}$  defined as the internuclear distance of each A-B bond and  $C=2c'_{B-B}$  defined as the internuclear distance of the two terminal B atoms, the bond angle between the A-B bonds is given by the law of cosines is

$$\theta = \cos^{-1}\left(\frac{2(2c'_{A-B})^2 - (2c'_{B-B})^2}{2(2c'_{A-B})^2}\right)$$

10

- 246. The system of claim 245 wherein the specie comprises more than two bonds with one A-B bound along an axis defined as the vertical or z-axis and any two A-B bonds form an isosceles triangle; the angle of the bonds from the defined axis is determined from the geometrical relationships:
- the distance  $d_{origin-B}$  from the origin to the nucleus of a terminal B atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60^{\circ}};$$

the height along the z-axis from the origin to A nucleus  $d_{height}$  is given by

$$d_{height} = \sqrt{\left(2c'_{A-B}\right)^2 - \left(d_{origin-B}\right)^2}$$
, and

the angle  $\theta_{\nu}$  of each A-B bond from the z-axis is given by

$$\theta_{v} = \tan^{-1} \left( \frac{d_{origin-B}}{d_{height}} \right).$$

247. The system of claim 246 wherein the vibrational energies are determined by the forces between the central field and the electrons and those between the nuclei; said electron-central-field force and its derivative are given by

25 
$$f(R) = -c_{BO} \frac{c_1 c_2 e^2}{4\pi\epsilon_0 R^3}$$

and

$$f'(a) = 2c_{BO} \frac{c_1 c_2 e^2}{4\pi \varepsilon_0 R^3};$$

said nuclear repulsion force and its derivative are given by

$$f(2c') = \frac{e^2}{8\pi\varepsilon_0 (2c')^2}$$

and

$$f'(2c') = -\frac{e^2}{4\pi\varepsilon_0 (2c')^3}$$

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO}\frac{c_1c_2e^2}{4\pi\varepsilon_0R^3} - \frac{e^2}{8\pi\varepsilon_0(2c')^2}}{\mu}}$$

where  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  is the reduced mass of the nuclei, R is b or a,  $c_{BO}$  is the bond-order

factor which is 1 for a single bond, 4 for a double bond, and 9 for a triplet bond,  $c_1$  is the 10 fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie, and

- $c_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.
- 248. The system of claim 247 wherein the transition-state vibrational energy,  $E_{vib}(0)$ , 15 given by Planck's equation is:

$$E_{vib}(0) = \hbar \omega$$

249. The system of claim 248 wherein the energy  $\tilde{v}_{v}$  of state v is given by

$$\tilde{v}_v = v\omega_0 - v(v-1)\omega_0 x_0$$
,  $v = 0,1,2,3...$ 

20 where

$$\omega_0 x_0 = \frac{hc\omega_0^2}{4D_0}$$

 $\omega_0$  is the frequency of the  $\upsilon = 1 \rightarrow \upsilon = 0$  transition, and  $D_0$  is the bond dissociation energy.

250. The system of claim 249 wherein  $\omega_0$  is given by

$$\omega_0 = E_{vib}(0) - 2\omega_0 x_0$$
, and

$$\omega_0 = E_{vib}(0) - 2\frac{hc\omega_0^2}{4D_0}$$

such that

5 
$$\omega_0^2 + \frac{2D_0}{hc}\omega_0 - \frac{2D_0}{hc}E_{vib}(0) = 0$$
, and 
$$\omega_0 = \frac{-\frac{2D_0}{hc} \pm \sqrt{\left(\frac{2D_0}{hc}\right)^2 + 4\frac{2D_0}{hc}E_{vib}(0)}}{2}$$

251. The system of claim 250 wherein  $B_e$ , the rotational parameter, for A-B is given by:

$$B_e = \frac{\hbar^2}{2I_e hc}$$

- 10 where  $I = \mu r^2$ , r = 2c', and  $\mu$  is the reduced mass.
- 252. The system of claim 251 wherein the vibrational energy levels of the A-A and A-B bonds of the specie are solved as sets of coupled atomic harmonic oscillators wherein each atom of a chain of bonds is further coupled to at least one additional harmonic
  15 oscillators by using the Lagrangian, the differential equation of motion, and the eigenvalue

solutions wherein the spring constants are derived from the central forces.

- 253. The system of claim 252 wherein the vibrational energy levels of the C-C bonds of  $C_nH_{2n+2}$  are solved as n-1 sets of coupled carbon harmonic oscillators wherein each carbon
- 20 is further coupled to two or three equivalent *H* harmonic oscillators by using the Lagrangian, the differential equation of motion, and the eigenvalue solutions wherein the spring constants are derived from the central forces.
  - 254. The system of claim 253 wherein  $E_D(C_nH_{2n+2})$ , the total bond dissociation energy of
- 25  $C_n H_{2n+2}$ , is given as the sum of the energy components due to the two methyl groups, n-2 methylene groups, and n-1 C-C bonds.

255. The system of claim 254 wherein the total bond dissociation energy of  $C_n H_{2n+2}$  is given by

$$E_D(C_n H_{2n+2}) = E_D(C - C)_{n-1} + 2E_{D_{alkans}}(^{12}CH_3) + (n-2)E_{D_{alkans}}(^{12}CH_2)$$
$$= (n-1)(4.32754 \text{ eV}) + 2(12.49186 \text{ eV}) + (n-2)(7.83016 \text{ eV})$$

wherein the calculated and measured values and constants recited in the equations herein can 5 be adjusted, for example, up to  $\pm 10\%$ , if desired.

- 256. The system of claim 255 wherein the exact solution for the dimensional parameters, charge density functions, and energies of molecules are determined using the results for the determination of  $C_n H_{2n+2}$  and the functional groups as basis sets that are linearly combined.
- 257. The system of claim 256 wherein one or more of the hydrogen atoms of the solution for  $C_nH_{2n+2}$  are substituted with one or more of the previously solved functional groups or derivative functional groups to give the parameters of a desired molecule.
- 15 258. The system of claim 257 wherein the parameters of a given molecule are given by energy matching each group to  $C_nH_{2n+2}$ .
  - 259. The system of claim 258 wherein substitution of one or more H's of  $C_nH_{2n+2}$  with functional groups from the list of  $CH_3$ , other  $C_nH_{2n+2}$  groups,  $H_2C=CH_2$ ,  $HC\equiv CH$ , F,
- 20 Cl, O, OH, NH, NH<sub>2</sub>, CN, NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, and C<sub>6</sub>H<sub>6</sub> give the solutions of branched alkanes, alkenes, and alkynes, alkyl halides, ethers, alcohols, amides, amines, nitriles, alkyl nitrosos, alkyl nitrates, aldehydes, ketones, carboxylic acids, esters, and substituted aromatics.
- 25 260. A composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms,
- 30 orbital intercept distances and angles,

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charge-density functions of atomic, hybridized, and molecular orbitals,
the bond distance, bond angle, and bond energy being calculated from physical solutions of
the charge, mass, and current density functions of atoms and atomic ions, which solutions are
derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate
5 under acceleration.

- 261. A composition of matter according to claim 260, wherein the novel property is a new pharmaceutical use.
- 10 262. A composition of matter according to claim 261 that is novel, wherein the novel property is stability at room temperature of a new arrangement of atoms or ions.
  - 263. A novel composition of matter discovered by calculating at least one of a bond distance between two of the atoms,
- a bond angle between three of the atoms, and
  a bond energy between two of the atoms,
  orbital intercept distances and angles,
  charge-density functions of atomic, hybridized, and molecular orbitals,
  the bond distance, bond angle, and bond energy being calculated from physical solutions of
  the charge, mass, and current density functions of atoms and atomic ions, which solutions are
  derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate
  - 264. A system of determining at least one of

under acceleration.

- a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals,
- 30 wherein the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration.

- 265. The system of claim 264, further comprising discovering a new composition of matter.
- 5 266. The system of claim 1, wherein the nature of said specie includes the nature of a chemical bond thereof.
  - 267. The system of claim 1, wherein at least one bond angle between three atoms is computed and displayed.

- 268. The system of claim 1, wherein at least one bond distance between two atoms is computed and displayed.
- 269. The system of claim 1, wherein at least one geometric component is computed and 15 displayed.
  - 270. The system of claim 1, wherein at least one potential energy between an electron and a nucleus is computed.
- 20 271. The system of claim 1, wherein at least one potential energy between two nuclei is computed.
  - 272. The system of claim 1, wherein at least one kinetic energy of an electron is computed.
- 25 273. The system of claim 1, wherein at least one magnetic energy between electrons is computed.
  - 274. The system of claim 1, wherein at least one total energy of a bond is computed.
- 30 275. The system of claim 1, wherein at least one change in atomic energy between atoms due to bonding is computed.

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- 276. The system of claim 1, further comprising at least one database of functional groups and at least one database of molecules, molecular ions, and/or molecular radicals, characterized in that the functional groups, molecules, molecular ions, and molecular radicals having the nature of their chemical bonds computed by the Maxwillian solutions of charge, mass, and current density, or both databases being combined into one database or split into multiple databases, and the processing means being in communication with the databases or combined database.
- 277. The system of claim 1, further comprising at least one database of functional groups10 having the nature of their chemical bonds computed by the Maxwillian solutions of charge, mass, and current density.
- 278. The system of claim 276, further comprising means for selecting a desired first functional group, characterized in that the selected functional group is displayed with open bonds being displayed, means for selecting an open bond, means for selecting a second functional group to be bound to the first functional group, characterized in that the second functional group is displayed with open bonds being displayed, means for selecting an open bond on the second functional group, and means for combining the selected bonds, whereby at least a portion of a desired molecule is displayed.

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- 279. The system of claim 276, further comprising selecting and combining functional groups until a desired molecule is displayed.
- 280. The system of claim 277, further comprising means for selecting a desired first
  25 functional group, characterized in that the selected functional group is displayed with open bonds being displayed, means for selecting an open bond, means for selecting a second functional group to be bound to the first functional group, characterized in that the second functional group is displayed with open bonds being displayed, means for selecting an open bond on the second functional group, and means for combining the selected bonds, whereby
  30 at least a portion of a desired molecule is displayed.
  - 281. The system of claim 277, further comprising selecting and combining functional groups until a desired molecule is displayed.

- 282. The system of claim 1, further comprising a means for inputting the chemical structure of a desired molecule and parsing the inputted molecule into functional groups.
- 5 283. The system of claim 282, further comprising a database of functional groups having the nature of their chemical bonds computed by the Maxwillian solutions of charge, mass, and current density, characterized in that the processing means combines the functional groups and the desired molecule is displayed.
- 10 284. The system of claim 282, wherein the chemical structure is imputed using a Simplified Molecular Input Line Entry System.
  - 285. The system of claim 283, wherein the chemical structure is imputed using a Simplified Molecular Input Line Entry System.

- 286. The system of claim 282, wherein the Simplified Molecular Input Line Entry System is SMILES.
- 287. The system of claim 283, wherein the Simplified Molecular Input Line Entry System 20 is SMILES.
  - 288. The system according to claim 1, wherein the force generalized constant k' of a  $H_2$ type ellipsoidal MO due to the equivalent of two point charges at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \tag{15.1}$$

25 where  $C_1$  is the fraction of the  $H_2$ -type ellipsoidal molecular orbital basis function of a chemical bond of the specie and  $C_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond.

289. The system according to claim 1, wherein the distance from the origin of the MO to each focus c' is given by:

$$c' = a \sqrt{\frac{\hbar^2 4\pi \varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (15.2)

5

the internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.3}$$

the length of the semiminor axis of the prolate spheroidal MO b = c is given by

$$10 b = \sqrt{a^2 - c'^2} (15.4)$$

and, the eccentricity, e, is

$$e = \frac{c'}{a} \tag{15.5}.$$

15

290. The system according to claim 289, wherein a potential energy of the electrons in the central field of the nuclei at the foci is

$$V_{e} = n_{1}c_{1}c_{2}\frac{-2e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2}-b^{2}}}\ln\frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}$$
(15.6)

where  $n_1$  is the number of equivalent bonds of the MO for functional groups and in the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor, which is 1 for a single bond, 4 for an independent double bond and 9 for an independent triplet bond.

291. The system according to claim 1, wherein the potential energy of the two nuclei is

25 
$$V_{p} = n_{1} \frac{e^{2}}{8\pi\varepsilon_{o} \sqrt{a^{2} - b^{2}}}$$
 (15.7).

292. The system according to claim 1, wherein the kinetic energy of the electrons is

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$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(15.8)

where  $n_1$  is the number of equivalent bonds of the MO for functional groups and in the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor, which is 1 for a single bond, 4 for an independent 5 double bond and 9 for an independent triplet bond.

293. The system according to claim 1, wherein the energy,  $V_m$ , of the magnetic force between the electrons is

$$V_{m} = n_{1}c_{1}c_{2} \frac{-\hbar^{2}}{4m_{c}a\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}}$$
(15.9)

- 10 where  $n_1$  is the number of equivalent bonds of the MO for functional groups and in the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor, which is 1 for a single bond, 4 for an independent double bond and 9 for an independent triplet bond.
- 15 294. The system according to claim 1, wherein total energy of the  $H_2$ -type prolate spheroidal MO,  $E_T(H_2MO)$ , is given by the sum of the energy terms:

$$E_T(H_2MO) = V_e + T + V_m + V_p \tag{15.10}$$

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right]$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right]$$
(15.11)

where  $n_1$  is the number of equivalent bonds of the MO for functional groups and in the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor, which is 1 for a single bond, 4 for an independent double bond and 9 for an independent triplet bond.

295. The system according to claim 1, wherein the total energy  $E_T(atom, msp^3)$  (m is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one AO shell according to the formula:

5 
$$E_T(atom, msp^3) = -\sum_{m=1}^{n} IP_m$$
 (15.12)

where  $IP_m$  is the m th ionization energy (positive) of the atom.

296. The system according to claim 295, wherein the radius  $r_{msp}$ , of the hybridized shell is given by:

10 
$$r_{msp^3} = \sum_{q=Z-n}^{Z-1} \frac{-(Z-q)e^2}{8\pi\varepsilon_0 E_T \left(atom, msp^3\right)}$$
 (15.13).

297. The system according to claim 295, wherein the Coulombic energy  $E_{Coulomb}(atom, msp^3)$  of the outer electron of the atom  $msp^3$  shell is given by

$$E_{Coulomb}\left(atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}}$$
(15.14).

15

298. The system of claim 296, wherein in the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius r of the AO electron:

20 
$$E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} = \frac{8\pi\mu_o \mu_B^2}{r^3}$$
 (15.15)

then, the energy  $E(atom, msp^3)$  of the outer electron of the  $atom msp^3$  shell is given by the sum of  $E_{Coulomb}(atom, msp^3)$  and E(magnetic):

$$E(atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r^{3}}$$
(15.16).

299. The system according to claim 295, wherein the total energy  $E_T$  (mol.atom, msp<sup>3</sup>) (m is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:

$$E_{T}(mol.atom, msp^{3}) = E(atom, msp^{3}) - \sum_{m=2}^{n} IP_{m}$$
(15.17)

where  $IP_m$  is the *m* th ionization energy (positive) of the atom and the sum of  $-IP_1$  plus the hybridization energy is  $E(atom, msp^3)$ .

10 300. The system of claim 299, wherein the radius  $r_{msp^3}$  of the hybridized shell is given by:

$$r_{msp}^{2} = \left(\sum_{q=Z-n}^{Z-1} (Z-q) - s(0.25)\right) \frac{-e^{2}}{8\pi\varepsilon_{0}E_{T}(mol.atom, msp^{3})}$$
(15.18)

where s = 1, 2, 3 for a single, double, and triple bond, respectively.

301. The system of claim 299, wherein the Coulombic energy  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> shell is given by

$$E_{Coulomb}\left(mol.atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}}$$
(15.19).

302. The system of claim 298, wherein in the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius r of the AO electron given by Eq. (15.15). Then, the energy  $E(mol.atom, msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by the sum of  $E_{Coulomb}$  ( $mol.atom, msp^3$ ) and E(magnetic):

$$E(mol.atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r^{3}}$$
(15.20)

 $E_T(atom-atom,msp^3)$ , the energy change of each  $atom\ msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(mol.atom,msp^3)$  and  $E(atom,msp^3)$ :

$$E_{T}\left(atom-atom,msp^{3}\right)=E\left(mol.atom,msp^{3}\right)-E\left(atom,msp^{3}\right) \tag{15.21}$$

5

303. The system of claim 295, wherein  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) is one of:

$$E_{Coulomb}\left(C_{ethylene},2sp^3\right),\;E_{Coulomb}\left(C_{ethane},2sp^3\right),\;E_{Coulomb}\left(C_{acetylene},2sp^3\right),\;$$
 and  $E_{Coulomb}\left(C_{alkane},2sp^3\right);\;$ 

$$E_{Coulomb}(atom, msp^3)$$
 is one of  $E_{Coulomb}(C, 2sp^3)$  and  $E_{Coulomb}(Cl, 3sp^3)$ ;

10  $E(mol.atom, msp^3)$  is one of  $E(C_{ethylene}, 2sp^3)$ ,  $E(C_{ethane}, 2sp^3)$ ,

$$E(C_{acetylene}, 2sp^3) E(C_{alkane}, 2sp^3);$$

 $E(atom, msp^3)$  is one of and  $E(C, 2sp^3)$  and  $E(Cl, 3sp^3)$ ;

 $E_T(atom-atom, msp^3)$  is one of  $E(C-C, 2sp^3)$ ,  $E(C=C, 2sp^3)$ , and

$$E(C \equiv C, 2sp^3);$$

15

atom msp<sup>3</sup> is one of C2sp<sup>3</sup>, Cl3sp<sup>3</sup>

$$E_T(atom-atom(s_1),msp^3)$$
 is  $E_T(C-C,2sp^3)$  and  $E_T(atom-atom(s_2),msp^3)$  is  $E_T(C=C,2sp^3)$ , and

 $r_{msp}$ , is one of  $r_{C2sp^3}$ ,  $r_{ethane2sp^3}$ ,  $r_{ethylene2sp^3}$ ,  $r_{acetylene2sp^3}$ ,  $r_{alkane2sp^3}$ , and  $r_{Cl3sp^3}$ .

In the case of the  $C2sp^3$  HO, the initial parameters (Eqs. (14.142-14.146)) are

$$r_{2sp^3} = \sum_{n=2}^{3} \frac{(Z-n)e^2}{8\pi\varepsilon_0 \left(e148.25751 \ eV\right)} = \frac{10e^2}{8\pi\varepsilon_0 \left(e148.25751 \ eV\right)} = 0.91771a_0$$
 (15.22)

$$E_{Coulomb}\left(C, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2,p^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.91771a_{0}} = -14.82575 \ eV \tag{15.23}$$

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_o \mu_B^2}{(0.84317a_0)^3} = 0.19086 \ eV$$
 (15.24)

$$E(C,2sp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(r_{3})^{3}}$$

$$= -14.82575 \ eV + 0.19086 \ eV$$

$$= -14.63489 \ eV$$
(15.25)

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

## 5 304. The system of claim 300, wherein

$$\sum_{q=Z-n}^{Z-1} (Z-q) = 10 \tag{15.26}$$

Equations (14.147) and (15.17) give

$$E_T(mol.atom, msp^3) = E_T(C_{ethane}, 2sp^3) = -151.61569 \ eV$$
 (15.27)

and using Eqs. (15.18-15.28), the final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}\left(C2sp^3\right)$ , and  $E\left(C2sp^3\right)$ , and

10 the resulting  $E_T\left(C \stackrel{BO}{-} C, C2sp^3\right)$  of the MO due to charge donation from the HO to the MO

where C - C refers to the bond order of the carbon-carbon bond for different values of the parameter s are given in Table 15.1.

Table 15.1:

15

MQ	s 1	s 2	$r_{C2sp^3}(a_0)$	$E_{Coulomb}\left(C2sp^3\right)$ (eV)	$E(C2sp^3)$	$E_T \left( C - C, C2sp^3 \right)$
Bond	1			Final	, ,	$L_{T}(C,Czsp)$
Order			Final		(eV)	(eV)
(BO)					Final	
I	1	0	0.87495	-15.55033	-15.35946	-0.72457
П	2	0	0.85252	-15.95955	-15.76868	-1.13379
Ш	3	0	0.83008	-16.39089	-16.20002	-1.56513
IV	4	0	0.80765	-16.84619	-16.65532	-2.02043

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm 10\%$ , if desired.

305. The system of claim 295, wherein a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the energy  $E(mol.atom, msp^3)$  of the outer electron of the atom  $msp^3$  shell of each bonding atom is the average of  $E(mol.atom, msp^3)$  for two different values of s:

$$E(mol.atom, msp^3) = \frac{E(mol.atom(s_1), msp^3) + E(mol.atom(s_2), msp^3)}{2}$$
(15.28).

306. The system of claim 305, wherein in the case,  $E_T(atom-atom,msp^3)$ , the energy change of each  $atom\ msp^3$  shell with the formation of each atom-atom-bond MO, is average for two different values of s:

10 
$$E_T(atom-atom, msp^3) = \frac{E_T(atom-atom(s_1), msp^3) + E_T(atom-atom(s_2), msp^3)}{2}$$
 (15.29).

307. The system of claim 305, wherein a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO comprises another AO or HO having a single bond order or a mixed bond order, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO, and in general, E<sub>T</sub> (atom – atom, msp³), the energy change of each atom msp³ shell with the formation of each atom-atom-bond MO, is a weighted
20 linear sum for different values of s that matches the energy of the bonded MOs, HOs, and AOs:

$$E_T\left(atom-atom, msp^3\right) = \sum_{n=1}^{N} c_{s_n} E_T\left(atom-atom(s_n), msp^3\right)$$
 (15.30)

where  $c_{s_n}$  is the multiple of the BO of  $s_n$ . The radius  $r_{msp^3}$  of the atom  $msp^3$  shell of each bonding atom is given by the Coulombic energy using the initial energy  $E_{Coulomb}$  (atom,  $msp^3$ ) and  $E_T$  (atom – atom,  $msp^3$ ), the energy change of each atom  $msp^3$  shell with the formation of each atom-atom-bond MO:

$$r_{msp^3} = \frac{-e^2}{8\pi\varepsilon_0 a_0 \left(E_{Coulonb}\left(atom, msp^3\right) + E_T\left(atom - atom, msp^3\right)\right)}$$
where  $E_{Coulomb}\left(C2sp^3\right) = -14.825751 \ eV$ . (15.31)

- 5 308. The system of claim 307, wherein the Coulombic energy  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> shell is given by Eq. (15.19).
- 309. The system of claim 308, wherein in the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy  $E(mol.atom, msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by the sum of  $E_{Conlomb}$  ( $mol.atom, msp^3$ ) and E(magnetic) (Eq. (15.20)).
- 15 310. The system of claim 308, wherein,  $E_T(atom-atom,msp^3)$ , the energy change of each atom  $msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(mol.atom,msp^3)$  and  $E(atom,msp^3)$  given by Eq. (15.21).
- 20 311. The system of claim 310, wherein using the equation (15.23) for  $E_{Coulomb}(C, 2sp^3)$  in equation (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to + 10%, if desired.
  - 312. The system of claim 295, wherein the radius  $r_{mol2sp}$ , of the  $C2sp^3$  HO of a carbon atom of a given specie is calculated using Eq. (14.514) by considering

 $\sum E_{T_{mol}}(MO, 2sp^3)$ , the total energy donation to each bond with which it participates in bonding.

5 313. The system of claim 1, wherein equation for the radius is given by

$$r_{mol 2sp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(E_{Coulomb}\left(C, 2sp^{3}\right) + \sum E_{T_{mol}}\left(MO, 2sp^{3}\right)\right)}$$

$$= \frac{e^{2}}{8\pi\varepsilon_{0} \left(e14.825751 \ eV + \sum \left|E_{T_{mol}}\left(MO, 2sp^{3}\right)\right|\right)}$$
(15.32).

- 314. The system of 295, wherein the Coulombic energy  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> shell is given by Eq. (15.19).
- 315. The system of claim 295, in the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy E(mol.atom, msp³) of the outer
  electron of the atom msp³ shell is given by the sum of E<sub>Coulomb</sub> (mol.atom, msp³) and E(magnetic) (Eq. (15.20)).
- 316. The system of claim 315, wherein for the C2sp³ HO of each methyl group of an alkane contributes -0.92918 eV (Eq. (14.513)) to the corresponding single C-C bond;
  20 the corresponding C2sp³ HO radius is given by Eq. (14.514). The C2sp³ HO of each methylene group of C<sub>n</sub>H<sub>2n+2</sub> contributes -0.92918 eV to each of the two corresponding C-C bond MOs, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.
- 25 317. The system of claim 316, wherein the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are

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$$r_{alkaneC_{undoplens} 2sp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(E_{Coulomb} \left(C, 2sp^{3}\right) + \sum E_{T_{elkans}} \left(methylene \ C - C, 2sp^{3}\right)\right)}$$

$$= \frac{e^{2}}{8\pi\varepsilon_{0} \left(e14.825751 \ eV + e0.92918 \ eV + e0.92918 \ eV\right)}$$

$$= 0.81549a_{0}$$

$$(15.33)$$

$$E_{Coulomb} \left(C_{methylene} 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(0.81549a_{0}\right)} = -16.68412 \ eV \ (15.34)$$

$$E\left(C_{methylene} 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(0.81549a_{0}\right)} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2} \left(0.84317a_{0}\right)^{3}} = -16.49325 \ eV \ (15.35)$$

- 5 wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm 10\%$ , if desired.
- 318. The system of claim 316, wherein in the determination of the parameters of functional groups, heteroatoms bonding to C2sp³ HOs to form MOs are energy matched to the
   C2sp³ HOs, the radius and the energy parameters of a bonding heteroatom are given by the same equations as those for C2sp³ HOs.
  - 319. The system of claim 318, wherein using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO,
- $r_{Atom.HO.AO}$ ,  $E_{Coulomb}$  ( $mol.atom, msp^3$ ), and  $E(C_{mol}2sp^3)$  are calculated using  $\sum E_{T_{group}}(MO,2sp^3)$ , the total energy donation to each bond with which an atom participates in bonding corresponding to the values of  $E_T(C^{BO}-C,C2sp^3)$  of the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2 and the final values of  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}$  ( $mol.atom, msp^3$ ), and  $E(C_{mol}2sp^3)$  calculated using
- the values of  $E_T \left( C \stackrel{BO}{-} C, C2sp^3 \right)$  given in Tables 15.1 and 15.2 are shown in Tables 15.3A and 15.3B in the specification, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

15

- 320. The system of claim 319, wherein the energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO.
- 321. The system of claim 320, wherein the force constant k' (Eq. (15.1)) is used to determine the ellipsoidal parameter c' (Eq. (15.2)) of the each H<sub>2</sub>-type-ellipsoidal-MO in terms of the central force of the foci, c' is substituted into the energy equation (from Eq. (15.11))) which is set equal to n<sub>1</sub> times the total energy of H<sub>2</sub> where n<sub>1</sub> is the number of equivalent bonds of the MO and the energy of H<sub>2</sub>, -31.63536831 eV, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

322. The system of claim 321, wherein the energy equation and the relationship between the axes, the dimensions of the MO are solved, the energy equation has the semimajor axis a as it only parameter, the solution of the semimajor axis a allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)),

- and the parameter solutions then allow for the component and total energies of the MO to be determined.
  - 323. The system of claim 1, wherein the total energy,  $E_T(H_2MO)$ , is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus  $E_T(AO/HO)$ :

25 
$$E_{T}(H_{2}MO) = V_{e} + T + V_{m} + V_{p} + E_{T}(AO/HO) \quad (15.36)$$

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_{T}(AO/HO)$$

$$(15.37)$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type

ellipsoidal MO basis function of a chemical bond of the group,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and  $E_T(AO/HO)$  is the total energy comprising the difference of the energy E(AO/HO) of at least one atomic or hybrid orbital to which the MO is energy matched and 5 any energy component  $\Delta E_{H,MO}(AO/HO)$  due to the AO or HO's charge donation to the MO.

- 324. The system of claim 323, wherein  $E_T(AO/HO) = E(AO/HO) \Delta E_{H,MO}(AO/HO) \quad (15.38)$
- 10 325. The system of claim 324, wherein as specific examples,  $E_T(AO/HO)$  is one from the group of

$$E_T(AO/HO) = E(O2p \text{ shell}) = -E(\text{ionization}; O) = -13.6181 \text{ eV};$$

$$E_T(AO/HO) = E(N2p \text{ shell}) = -E(\text{ionization}; N) = -14.53414 \text{ eV};$$

$$E_T(AO/HO) = E(C, 2sp^3) = -14.63489 eV;$$

15 
$$E_T(AO/HO) = E_{Coulomb}(Cl, 3sp^3) = -14.60295 eV;$$

$$E_T(AO/HO) = E(ionization; C) + E(ionization; C^+);$$

$$E_T(AO/HO) = E(C_{ethome}, 2sp^3) = -15.35946 \text{ eV};$$

$$E_T(AO/HO) = +E(C_{ethylene}, 2sp^3) - E(C_{ethylene}, 2sp^3);$$

$$E_T(AO/HO) = E(C, 2sp^3) - 2E_T(C = C, 2sp^3) = -14.63489 \ eV - (-2.26758 \ eV);$$

20 
$$E_T(AO/HO) = E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) = 16.20002 \ eV;$$

$$E_T(AO/HO) = E(C, 2sp^3) - 2E_T(C \equiv C, 2sp^3) = -14.63489 \ eV - (-3.13026 \ eV);$$

$$E_T(AO/HO) = E(C_{benzene}, 2sp^3) - E(C_{benzene}, 2sp^3);$$

$$E_T(AO/HO) = E(C, 2sp^3) - E_T(C = C, 2sp^3) = -14.63489 \text{ eV} - (-1.13379 \text{ eV})$$
, and

$$E_T(AO/HO) = E(C_{alkane}, 2sp^3) = -15.56407 \, eV$$
, wherein the calculated and measured

values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

326. The system of claim 1, wherein to solve the bond parameters and energies,

$$c' = a \sqrt{\frac{\hbar^2 4\pi \varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}} \text{ (Eq. (15.2)) is substituted into } E_T(H_2MO) \text{ to give}$$

$$E_T(H_2MO) = -\frac{n_1 e^2}{8\pi \varepsilon_o \sqrt{a^2 - b^2}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right] + E_T(AO/HO)$$

$$= -\frac{n_1 e^2}{8\pi \varepsilon_0 c'} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_T(AO/HO)$$

$$= -\frac{n_1 e^2}{8\pi \varepsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}}}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} - 1 \right] + E_T(AO/HO)$$

(15.39)

wherein the total energy is set equal to  $E(basis\ energies)$  which in the most general case is given by the sum of a first integer  $n_1$  times the total energy of  $H_2$  minus a second integer  $n_2$  times the total energy of H, minus a third integer  $n_3$  times the valence energy of E(AO) (e.g.  $E(N) = -14.53414\ eV$ ) where the first integer can be 1,2,3..., and each of the second and third integers can be 0,1,2,3....

10

327. The system of claim 326, wherein

$$E(basis\ energies) = n_1(-31.63536831\ eV) - n_2(-13.605804\ eV) - n_3E(AO)$$
(15.40)

in the case that the MO bonds two atoms other than hydrogen,  $E(basis\ energies)$  is  $n_1$  times 15 the total energy of  $H_2$  where  $n_1$  is the number of equivalent bonds of the MO and the energy of  $H_2$ , -31.63536831 eV, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

$$E(basis\ energies) = n_1(-31.63536831\ eV)$$
 (15.41)

 $E_T(\mu_2MO)$ , is set equal to  $E(basis\ energies)$ , and the semimajor axis a is solved.

20

328. The system of claims 289 or 326, wherein the semimajor axis a is solved from the equation of the form:

$$-\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}\left[c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right)\ln\frac{a+\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a-\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}-1\right]+E_{T}\left(AO/HO\right)=E(basis\ energies)$$
(15.42)

The distance from the origin of the  $H_2$ -type-ellipsoidal-MO to each focus c', the internuclear distance 2c', and the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO 5 b=c are solved from the semimajor axis a using Eqs. (15.2-15.4).

- 329. The system of claim 328, wherein the component energies are given by Eqs. (15.6-15.9) and (15.39).
- 10 330. The system of claim 323, wherein the total energy of the MO of the functional group,  $E_T(MO)$ , is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms and  $E_T(atom-atom, msp^3.AO)$ , the change in the energy of the AOs or HOs upon forming the bond.

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- 331. The system of claim 330, wherein from Eqs. (15.39-15.40),  $E_T(MO)$  is  $E_T(MO) = E(basis\ energies) + E_T(atom-atom, msp^3.AO) \qquad (15.43)$
- 332. The system of claim 331, wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the sum of the Doppler,  $\overline{E}_{D}$ , and average vibrational kinetic energies,  $\overline{E}_{Kvib}$ :

$$\overline{E}_{osc} = n_1 \left( \overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left( E_{hv} \sqrt{\frac{2\overline{E}_K}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.44)

where  $n_1$  is the number of equivalent bonds of the MO, k is the spring constant of the equivalent harmonic oscillator, and  $\mu$  is the reduced mass.

25

333. The system of claim 332, wherein the angular frequency of the reentrant oscillation in the transition state corresponding to  $\overline{E}_{D}$  is determined by the force between the central

field and the electrons in the transition state.

334. The system of claim 333, wherein the force and its derivative are given by

$$f(R) = -c_{BO} \frac{C_{1o} C_{2o} e^2}{4\pi \varepsilon_o R^3}$$
 (15.45)

5 and

$$f'(a) = 2c_{BO} \frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}$$
 (15.46)

such that the angular frequency of the oscillation in the transition state is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\epsilon_0 R^3}}{m_e}}$$
(15.47)

where R is the semimajor axis a or the semiminor axis b depending on the eccentricity of the bond that is most representative of the oscillation in the transition state,  $c_{BO}$  is the bond-order factor which is 1 for a single bond and when the MO comprises  $n_1$  equivalent single bonds as in the case of functional groups,  $c_{BO}$  is 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules and 9 for an independent triplet bond,  $C_{1o}$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and  $C_{2o}$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond. Typically,  $C_{1o} = C_1$  and  $C_{2o} = C_2$ , the kinetic energy,  $E_K$ , corresponding to  $\overline{E}_D$  is given by Planck's equation for functional groups:

$$\overline{E}_{K} = \hbar \omega = \hbar \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{0}R^{3}}}$$
 (15.48)

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335. The system of claim 334, wherein the Doppler energy of the electrons of the reentrant orbit is

$$\overline{E}_D \cong E_{h\nu} \sqrt{\frac{2\overline{E}_K}{m_e c^2}} = E_{h\nu} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}}{\frac{m_e}{m_e c^2}}}$$
(15.49)

 $\overline{E}_{osc}$  given by the sum of  $\overline{E}_{D}$  and  $\overline{E}_{Kvib}$  is

$$\overline{E}_{osc}(group) = n_1 \left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1 \left(E_{hv} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}}{m_e} + E_{vib}}\right)$$
(15.50)

 $E_{h\nu}$  of a group having  $n_1$  bonds is given by  $E_T(MO)/n_1$  such that

$$\overline{E}_{osc} = n_1 \left( \overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left( E_T \left( MO \right) / n_1 \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
(15.51)

5  $E_{T+osc}$  (Group) is given by the sum of  $E_{T}$  (MO) (Eq. (15.42)) and  $\overline{E}_{asc}$  (Eq. (15.51)):

$$\begin{split} E_{T+osc}\left(\textit{Group}\right) &= E_{T}\left(\textit{MO}\right) + E_{osc} \\ &= \begin{pmatrix} \frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right)\ln\frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1\right] \\ &= \begin{pmatrix} \frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right)\ln\frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1\right] \\ &+ E_{T}\left(AO/HO\right) + E_{T}\left(atom - atom, msp^{3}.AO\right) \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}} \\ \frac{1}{m_{e}} + \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}}} & \frac{1}{2\hbar\sqrt{\frac{k}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}{\mu}}} & \frac{1}{2\hbar\sqrt{\frac{k}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}}} & \frac{1}{2\hbar\sqrt{\frac{k}}} \end{pmatrix} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}}} & \frac{1}{2\hbar\sqrt{\frac{k}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}}} & \frac{1}{2\hbar\sqrt{\frac{k}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}}} & \frac{1}{2\hbar\sqrt{\frac{k}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}}} & \frac{1}{2\hbar\sqrt{\frac{k}}} \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2\hbar\sqrt{\frac{k}}} & \frac{1}{2\hbar\sqrt{\frac{k}}} \\ \frac{1}{2\hbar\sqrt{\frac{k}}} & \frac{1}{2\hbar\sqrt$$

$$= \left(E(basis\ energies) + E_T\left(atom-atom,msp^3.AO\right)\right)\left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{\frac{m_e}{m_e}}}\right] + n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

(15.52).

336. The system of claim 335, wherein the total energy of the functional group  $E_T(group)$  is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms,  $E(basis\ energies)$ , the change in the energy of the AOs or HOs upon forming the bond  $(E_T(atom-atom, msp^3.AO))$ , the energy of

oscillation in the transition state, and the change in magnetic energy with bond formation,  $E_{mag}$ .

337. The system of claim 336, wherein from Eq. (15.52), the total energy of the group  $E_{T}(Group)$  is

$$E_{T}(Group) = \left(E(basis\ energies) + E_{T}\left(atom - atom, msp^{3}.AO\right)\right) \left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{m_{e}}}\right] + n_{1}\overline{E}_{Kvib} + E_{mag}$$
(15.53).

10 338. The system of claim 337, wherein the change in magnetic energy  $E_{mag}$  which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by

$$E_{mag} = c_3 \frac{2\pi\mu_0 e^2 \hbar^2}{m^2 r^3} = c_3 \frac{8\pi\mu_0 \mu_B^2}{r^3}$$
 (15.54)

where  $r^3$  is the radius of the atom that reacts to form the bond and  $c_3$  is the number of electron pairs.

$$E_{T}(Group) = \left(E(basis\ energies) + E_{T}(atom-atom,msp^{3}.AO)\right) \left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{\frac{E_{Lvib}}{r^{3}}}}\right] + n_{1}\overline{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}}$$

$$(15.55).$$

339. The system of claim 338, wherein the total bond energy of the group  $E_D$  (Group) is the negative difference of the total energy of the group (Eq. (15.55)) and the total energy of the starting species given by the sum of  $c_4 E_{initial}$  ( $c_4 AO/HO$ ) and  $c_5 E_{initial}$  ( $c_5 AO/HO$ ):

$$E_{D}(Group) = -\left(E(basis\ energies) + E_{T}\left(atom - atom, msp^{3}.AO\right)\right)\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right] + n_{1}\overline{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r_{n}^{3}} - \left(c_{4}E_{Initial}\left(AO/HO\right) + c_{5}E_{Intitial}\left(c_{5}AO/HO\right)\right)$$
(15.56).

340. The system of claim 336, wherein in the case of organic molecules, the atoms of the
 functional groups are energy matched to the C2sp³ HO such that

$$E(AO/HO) = -14.63489 eV$$
 (15.57)

For examples of  $E_{mag}$  from previous sections:

$$E_{mag}\left(C2sp^{3}\right) = c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} = c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{\left(0.91771a_{0}\right)^{3}} = c_{3}0.14803 \ eV$$
 (15.58)

$$E_{mag}(O2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{a_0^3} = c_3 0.11441 \ eV$$
 (15.59)

10 
$$E_{mag}(N2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{(0.93084a_0)^3} = c_3 0.14185 \ eV (15.60).$$

341. The system of claim 340, wherein in the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.42) to arrive at a, the
15 remaining parameters are determined using Eqs. (15.1-15.5), the energies are given by Eqs. (15.52-15.59), and to meet the equipotential condition for the union of the H<sub>2</sub>-type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor c<sub>2</sub> of a H<sub>2</sub>-type ellipsoidal MO in principal Eqs. (15.42) and (15.52) may given by

20 (i) one: 
$$c_2 = 1$$
 (15.61)

(ii) the ratio that is less than one of  $13.605804 \, eV$ , the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the

Coulombic energy of the participating AO or HO of the atom,  $E_{Coulomb}$  (MO.atom, msp<sup>3</sup>) given by Eqs. (15.19) and (15.31-15.32). For  $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right| > 13.605804 \ eV$ :

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}} = \frac{13.605804\ eV}{\left|E_{Coulomb}\left(MO.atom, msp^{3}\right)\right|}$$
(15.62)

For  $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right| < 13.605804 \ eV$ :

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-BAOrBsp^{3}}}}{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}} = \frac{\left|E_{Coulomb}\left(MO.atom, msp^{3}\right)\right|}{13.605804 \, eV}$$
(15.63)

(iii) the ratio that is less than one of 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the valence energy, E(valence), of the participating AO or HO of the atom where E(valence) is the ionization energy or  $E(MO.atom, msp^3)$  given by Eqs. (15.20) and (15.31-15.32). For  $|E(valence)| > 13.605804 \ eV$ :

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B AorBsp^{3}}}} = \frac{13.605804 \ eV}{|E(valence)|} \ (15.64)$$

For |E(valence)| < 13.605804 eV:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}}{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}} = \frac{|E(valence)|}{13.605804\ eV}$$
 (15.65)

15

(iv) the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom,  $E_{Coulomb}$  (MO.atom, msp<sup>3</sup>) given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy, E(valence), of the participating AO or HO of a second atom to which the first is energy matched where E(valence) is the

ionization energy or  $E(MO.atom, msp^3)$  given by Eqs. (15.20) and (15.31-15.32). For  $|E_{Coulomb}(MO.atom, msp^3)| > E(valence)$ :

$$c_2 = \frac{\left| E(valence) \right|}{\left| E_{Coulomb} \left( MO.atom, msp^3 \right) \right|}$$
 (15.66)

For  $|E_{Coulomb}(MO.atom, msp^3)| < E(valence)$ :

$$c_{2} = \frac{\left| E_{Coulomb} \left( MO.atom, msp^{3} \right) \right|}{\left| E(valence) \right|}$$
 (15.67)

(v) the ratio that is less than one of the magnitude of the valence-level energies,  $E_n(valence)$ , of the AO or HO of the nth participating atom of two that are energy matched where E(valence) is the ionization energy or  $E(MO.atom, msp^3)$  given by Eqs. (15.20) and (15.31-15.32):

$$c_2 = \frac{E_1(valence)}{E_2(valence)}$$
 (15.68)

(vi) the factor that is the ratio of the hybridization factor  $c_2(1)$  of the valence AO or HO of a first atom and the hybridization factor  $c_2(2)$  of the valence AO or HO of a second atom to which the first is energy matched where  $c_2(n)$  is given by Eqs. (15.62-15.68); alternatively  $c_2$  is the hybridization factor  $c_2(1)$  of the valence AOs or HOs a first pair of atoms and the hybridization factor  $c_2(2)$  of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = \frac{c_2(1)}{c_2(2)} \qquad (15.69)$$

20

(vii) the factor that is the product of the hybridization factor  $c_2(1)$  of the valence AO or HO of a first atom and the hybridization factor  $c_2(2)$  of the valence AO or HO of a second atom to which the first is energy matched where  $c_2(n)$  is given by Eqs. (15.62-15.69); alternatively  $c_2$  is the hybridization factor  $c_2(1)$  of the valence AOs or HOs a first pair of

atoms and the hybridization factor  $c_2(2)$  of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2)$$
 (15.70)

The hybridization factor  $c_2$  corresponds to the force constant k (Eqs. (11.65) and (13.58)).

- 5 In the case that the valence or Coulombic energy of the AO or HO is less than 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), then  $C_2$  corresponding to k' (Eq. (15.1)) is given by Eqs. (15.62-15.70).
  - 342. The system of claim 341, wherein specific examples of the factors  $c_2$  and  $c_2$  of a
- $H_2$ -type ellipsoidal MO of Eq. (15.51) given in following sections are

$$c_{2}(C2sp^{3}HO \ to \ F) = \frac{E(C,2sp^{3})}{E(F)}c_{2}(C2sp^{3}HO) = \frac{-14.63489 \ eV}{-17.42282 \ eV}(0.91771) = 0.77087;$$

$$C_{2}(C2sp^{3}HO \ to \ CI) = \frac{E(CI)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-12.96764 \ eV}{-14.63489 \ eV}(0.91771) = 0.81317;$$

$$C_{2}(C2sp^{3}HO \ to \ Br) = \frac{E(Br)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-11.81381 \ eV}{-14.63489 \ eV}(0.91771) = 0.74081;$$

$$C_{2}(C2sp^{3}HO \ to \ I) = \frac{E(I)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-10.45126 \ eV}{-14.63489 \ eV}(0.91771) = 0.65537;$$

$$c_{2}(C2sp^{3}HO \ to \ O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-13.61806 \ eV}{-14.63489 \ eV}(0.91771) = 0.85395;$$

$$c_{2}(H \ to \ 1^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})} = \frac{-14.53414 \ eV}{-15.35946 \ eV} = 0.94627;$$

$$c_{2}(C2sp^{3}HO \ to \ N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-14.53414 \ eV}{-14.63489 \ eV}(0.91771) = 0.91140;$$

$$c_{2}(H \ to \ 2^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})} = \frac{-14.53414 \ eV}{-15.56407 \ eV} = 0.93383;$$

$$C_{2}(S3p \ to \ H) = \frac{E(S,3p)}{E(H)} = \frac{-10.36001 \ eV}{-13.60580 \ eV} = 0.76144;$$

20 
$$C_2(C2sp^3HO \text{ to S}) = \frac{E(S)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.64965;$$

$$c_{2}(O \text{ to } S3sp^{3} \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(S)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771);$$

$$= 1.20632$$

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \ eV}{-13.60580 \ eV} = 0.85045;$$

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}\left(0.85045\right) = 0.66951;$$

$$C_2 \left( S3sp^3 \text{ to } O \text{ to } C2sp^3HO \right) = \frac{E\left( S, 3sp^3 \right)}{E\left( O, 2p \right)} c_2 \left( C2sp^3HO \right)$$

$$= \frac{-11.52126 \ eV}{-13.61806 \ eV} \left( 0.91771 \right) ;$$

$$= 0.77641$$

$$c_{2}(O \text{ to } N2p \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(N)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}}(0.91771);$$

$$= 0.85987$$

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727;$$

$$C_2$$
 (benzeneC2sp<sup>3</sup>HO) =  $c_2$  (benzeneC2sp<sup>3</sup>HO) =  $\frac{13.605804 \text{ eV}}{15.95955 \text{ eV}}$  = 0.85252;

$$c_{2}(arylC2sp^{3}HO \text{ to } O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}}(0.85252)$$

$$= 0.79329$$

$$c_2(H \text{ to anline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171,$$

$$c_{2}(arylC2sp^{3}HO \text{ to } N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.85252)$$

$$= 0.84665$$

5

$$c_{2}(H \text{ to anline } N) = \frac{E(N)}{E(C,2sp^{3})} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171;$$

$$c_{2}(arylC2sp^{3}HO \text{ to } N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.85252) , \text{ and}$$

$$= 0.84665$$

$$C_{2}(S3p \text{ to aryl-type } C2sp^{3}HO) = \frac{E(S,3p)}{E(C,2sp^{3})} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700.$$

- wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.
- 343. The system of claim 1, wherein the parameters of the point of intersection of each
   H<sub>2</sub>-type ellipsoidal MO and the A-atom AO are determined from the polar equation of
   the ellipse:

$$r = r_0 \frac{1+e}{1+e\cos\theta'}$$
 (15.71).

344. The system of claim 343, wherein the radius of the A shell is  $r_A$ , and the polar radial coordinate of the ellipse and the radius of the A shell are equal at the point of intersection such that

$$r_{A} = (a-c')\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\theta'}$$
 (15.72).

345. The system of claim 344, wherein the polar angle  $\theta'$  at the intersection point is given by

20 
$$\theta' = \cos^{-1} \left( \frac{a}{c'} \left( (a - c') \frac{1 + \frac{c'}{a}}{a_0} - 1 \right) \right)$$
 (15.73).

346. The system of claim 345, wherein the angle  $\theta_{AAO}$  the radial vector of the A AO makes with the internuclear axis is

$$\theta_{AAO} = 180^{\circ} - \theta'$$
 (15.74).

347. The system of claim 345, wherein the distance from the point of intersection of the orbitals to the internuclear axis is the same for both component orbitals such that the angle  $\omega t = \theta_{H_0MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -

type ellipsoidal MO with the A radial vector obeys the following relationship:

$$r_A \sin \theta_{AAO} = b \sin \theta_{H_2MO} \tag{15.75}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{r_a \sin \theta_{AAO}}{b} \qquad (15.76).$$

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- 348. The system of claim 347, wherein the distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by  $d_{H_2MO} = a\cos\theta_{H_2MO}$  (15.77).
- 15 349. The system of claim 347, wherein the distance  $d_{AAO}$  along the internuclear axis from the origin of the A atom to the point of intersection of the orbitals is given by  $d_{AAO} = c' d_{H,MO} \qquad (15.78).$
- 350. The system of claim 1, wherein in ACB MO comprising a linear combination of C-A-bond and C-B-bond MOs where C is the general central atom and a bond is possible between the A and B atoms of the C-A and C-B bonds, the  $\angle ACB$  bond angle is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal A and B atoms is zero.
- 25 351. The system of claim 350, wherein the force constant k' of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_o}$$
 (15.79)

where  $C_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the specie which is 0.75 (Eq. (13.59)) for a terminal A-H (A is H or other atom) and 1

otherwise and  $C_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.42) and (15.52).

5 352. The system of claim 351, wherein the distance from the origin of the MO to each focus c' of the A-B ellipsoidal MO is given by:

$$c' = a \sqrt{\frac{\hbar^2 4\pi \varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (15.80).

353. The system of claim 351, wherein the internuclear distance is

- 354. The system of claim 351, wherein the length of the semiminor axis of the prolate spheroidal A-B MO b=c is given by Eq. (15.4).
- 15 355. The system of claim 351, wherein the component energies and the total energy, E<sub>T</sub> (H<sub>2</sub>MO), of the A-B bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of H<sub>2</sub> except that the terms based on charge are multiplied by c<sub>BO</sub>, the bond-order factor which is 1 for a single bond and when the MO comprises n<sub>1</sub> equivalent single bonds as in the case of functional groups. c<sub>BO</sub> is 4 for an independent double bond as in the case of the CO<sub>2</sub> and NO<sub>2</sub> molecules.
  - 356. The system of claim 355, wherein the kinetic energy term is multiplied by  $c'_{BO}$  which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond, the electron energy terms are multiplied by  $c_1$ , the fraction of the  $H_2$ -type ellipsoidal MO basis function of a terminal chemical bond which is 0.75 (Eq. (13.233)) for a terminal A-H (A is H or other atom) and 1 otherwise.

- 357. The system of claim 355, wherein the electron energy terms are further multiplied by  $c'_2$ , the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond.
- 5 358. The system of claim 350, wherein when A-B comprises atoms other than H,  $E_T(atom-atom, msp^3.AO)$ , the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give  $E_T(H_2MO)$ :

$$E_{T}(H_{2}MO) = \frac{-e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c'_{2} \left( 2c_{BO} - c'_{BO} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + E_{T} \left( atom - atom, msp^{3}.AO \right)$$
(15.82).

- 359. The system of claim 350, the radiation reaction force in the case of the vibration of A-B in the transition state corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei.
- 15 360. The system of claim 359, wherein the total energy that includes the radiation reaction of the A-B MO is given by the sum of  $E_T$  (H<sub>2</sub>MO) (Eq. (15.82)) and  $\overline{E}_{asc}$  given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240).
- 361. The system of claim 360, wherein the total energy  $E_T(A-B)$  of the A-B MO including the Doppler term is

$$E_{T}(A-B) = \begin{bmatrix} \left(\frac{-e^{2}}{8\pi\varepsilon_{0}c'}\left[c_{1}c'_{2}\left(2c_{BO}-c'_{BO}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] + E_{T}\left(atom-atom, msp^{3}.AO\right) \right] \\ \left[1+\sqrt{\frac{2\hbar\sqrt{\frac{C_{BO}\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right] + \frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_{1}c'_{2}e^{2}}{8\pi\varepsilon_{o}a^{3}} - \frac{c_{BO}e^{2}}{8\pi\varepsilon_{o}\left(a+c'\right)^{3}}}{\mu}}$$

$$(15.83)$$

where  $C_{1o}$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of the oscillatory transition state of the A-B bond which is 0.75 (Eq. (13.233)) in the case of H bonding to a central atom and 1 otherwise,  $C_{2o}$  is the factor that results in an equipotential energy match of

the participating at least two atomic orbitals of the transition state of the chemical bond, and  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  is the reduced mass of the nuclei given by Eq. (11.154).

362. The system of claim 361, wherein to match the boundary condition that the total energy of the A-B ellipsoidal MO is zero,  $E_T(A-B)$  given by Eq. (15.83) is set equal to zero and substitution of Eq. (15.81) into Eq. (15.83) gives

$$0 = \begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} & c_{1}c_{2}'\left(2c_{BO} - c'_{BO}\frac{a_{0}}{a}\right) \ln\frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \end{bmatrix} + E_{T}\left(atom - atom, msp^{3}.AO\right) \end{bmatrix}$$

$$\begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} & \frac{-e^{2}}{a-\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \\ \frac{-e^{2}}{a-\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} & \frac{-e^{2}}{a-\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \\ \frac{-e^{2}}{a-\sqrt{\frac{aa_{0}}{2C_$$

- 10 363. The system of claim 362, wherein the vibrational energy-term of Eq. (15.84) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)).
- 364. The system of claim 362, wherein the electron-central-field force and its derivative are given by

$$f(a) = -c_{BO} \frac{c_1 c_2' e^2}{4\pi \varepsilon_0 a^3}$$
 (15.85)

and

$$f'(a) = 2c_{BO} \frac{c_1 c_2' e^2}{4\pi \varepsilon_0 a^3}$$
 (15.86).

20 365. The system of claim 364, wherein the nuclear repulsion force and its derivative are given by

$$f(a+c') = \frac{e^2}{8\pi\varepsilon_o(a+c')^2}$$
 (15.87)

and

$$f'(a+c') = -\frac{e^2}{4\pi\varepsilon_o(a+c')^3}$$
 (15.88)

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_1c_2'e^2}{4\pi\epsilon_0a^3} - \frac{e^2}{8\pi\epsilon_0(a+c')^2}}$$
 (15.89).

5

The system of claim 365, wherein since both terms of  $\overline{E}_{asc} = \overline{E}_D + \overline{E}_{Kvib}$  are small due 366. to the large values of a and c', an approximation of Eq. (15.84) which is evaluated to determine the bond angles of functional groups is given by

$$0 = \begin{bmatrix} \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}} & c_1c_2'\left(2-\frac{a_0}{a}\right) \ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}} - 1 \\ \frac{2\hbar\sqrt{\frac{c_1e^2}{4\pi\varepsilon_0a^3}}}{\frac{m_e}{m_ec^2}} + \frac{1}{2}\hbar\sqrt{\frac{\frac{c_1e^2}{8\pi\varepsilon_0a^3} - \frac{e^2}{8\pi\varepsilon_0\left(a+\sqrt{\frac{aa_0}{2C_1C_2}}\right)}}{\mu}} \\ (15.90). \end{bmatrix}$$

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The system of claim 366, wherein from the energy relationship given by Eq. (15.90) 367. and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the A-B MO can be solved.

- 368. The system of claim 367, wherein Eq. (15.90) is solved by the reiterative technique using a computer.
- 369.
- The system of claim 366, wherein a factor  $c_2$  of a given atom in the determination of  $c_2'$  for calculating the zero of the total A-B bond energy is given by Eqs. (15.62-15.65). 20

370. The system of claim 369, wherein in the case of a H-H terminal bond of an alkyl or alkenyl group,  $c'_2$  is the ratio of  $c_2$  of Eq. (15.62) for the H-H bond which is one and  $c_2$  of the carbon of the corresponding C-H bond:

$$c_2' = \frac{1}{c_2(C2sp^3)} = \frac{13.605804 \, eV}{E_{Coulomb} \left(C - H \, C2sp^3\right)}$$
 (15.91)

- 5 wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.
  - 371. The system of claim 366, wherein in the case of the determination of the bond angle of the ACH MO comprising a linear combination of C-A-bond and C-H-bond MOs where A and C are general, C is the central atom, and c<sub>2</sub> for an atom is given by Eqs. (15.62-15.70), c'<sub>2</sub> of the A-H terminal bond is the ratio of c<sub>2</sub> of the A atom for the A-H terminal bond and c<sub>2</sub> of the C atom of the corresponding C-H bond:

$$c_2' = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)(msp^3))}$$
 (15.92).

example, up to  $\pm$  10%, if desired.

- 15 372. The system of claim 366, wherein in the case of the determination of the bond angle of the COH MO of an alcohol comprising a linear combination of C-O-bond and O-H-bond MOs where C, O, and H are carbon, oxygen, and hydrogen, respectively, c'<sub>2</sub> of the C-H terminal bond is 0.91771 since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162),
  20 respectively) that is energy matched to the C2sp³ HO, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for
- 373. The system of claim 366, wherein in the determination of the hybridization factor  $c'_2$ of Eq. (15.90) from Eqs. (15.62-15.70), the Coulombic energy,  $E_{Coulomb}$  (MO.atom, msp<sup>3</sup>), or the energy,  $E(MO.atom, msp^3)$ , the radius  $r_{A-B AorBsp^3}$  of the A or B AO or HO of the heteroatom of the A-B terminal bond MO such as the  $C2sp^3$  HO of a terminal C-C

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bond is calculated using Eq. (15.32) by considering  $\sum E_{T_{mol}}(MO, 2sp^3)$ , the total energy donation to each bond with which it participates in bonding as it forms the terminal bond.

- 374. The system of claim 373, wherein the Coulombic energy  $E_{Coulomb}$  (MO.atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> shell is given by Eq. (15.19).
  - 375. The system of claim 374, wherein in the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron, and the energy  $E(MO.atom, msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by the sum of  $E_{Coulomb}(MO.atom, msp^3)$  and E(magnetic) (Eq. (15.20)).
- 276. The system of claim 365, wherein in the specific case of the terminal bonding of two carbon atoms, the  $c_2$  factor of each carbon given by Eq. (15.62) is determined using the Coulombic energy  $E_{Coulomb}\left(C-C\ C2sp^3\right)$  of the outer electron of the  $C2sp^3$  shell given by Eq. (15.19) with the radius  $r_{C-C\ C2sp^3}$  of each  $C2sp^3$  HO of the terminal C-C bond calculated using Eq. (15.32) by considering  $\sum E_{T_{uel}}\left(MO,2sp^3\right)$ , the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy, 0.92918 eV (Eq. (14.513)), corresponding to the terminal C-C bond. The corresponding  $E_T\left(atom-atom,msp^3.AO\right)$  in Eq. (15.90) is  $E_T\left(C-C\ C2sp^3\right)=-1.85836\ eV$ , wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

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377. The system of claim 366, wherein in the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus,  $c'_2$  is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

$$c_2' = \frac{1}{2} \left( c_2' \left( atom \ 1 \right) + c_2' \left( atom \ 2 \right) \right)$$
 (15.93)

In the exemplary cases of C-C, O-O, and N-N where C is carbon:

$$c_{2}' = \frac{1}{2} \left( \frac{\frac{e^{2}}{8\pi\epsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\epsilon_{0}a_{0}}} + \frac{\frac{e^{2}}{8\pi\epsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\epsilon_{0}r_{A-A\,A_{1}AO/HO}}} \right)$$

$$= \frac{1}{2} \left( \frac{13.605804 \, eV}{E_{Coulomb} \left( A - A.A_{1}AO/HO \right)} + \frac{13.605804 \, eV}{E_{Coulomb} \left( A - A.A_{2}AO/HO \right)} \right)$$
(15.94)

In the exemplary cases of C-N, C-O, and C-S

5 
$$c_2' = \frac{1}{2} \left( \frac{13.605804 \, eV}{E_{Coulomb} \left( C - B \, C2sp^3 \right)} + c_2 \left( C \, to \, B \right) \right)$$
 (15.95)

where C is carbon and  $c_2(C \text{ to } B)$  is the hybridization factor of Eqs. (15.52) and (15.84) that matches the energy of the atom B to that of the atom C in the group.

- 378. The system of claim 363, wherein the corresponding  $E_T(atom-atom, msp^3.AO)$
- term in Eq. (15.90) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.56)) are

$$E_T(C-O\ C2sp^3.O2p) = -1.44915\ eV$$
;  $E_T(C-O\ C2sp^3.O2p) = -1.65376\ eV$ ;

$$E_T(C-N C2sp^3.N2p) = -1.44915 eV$$
;  $E_T(C-S C2sp^3.S2p) = -0.72457 eV$ ;

15 
$$E_T(O-O\ O2p.O2p) = -1.44915\ eV$$
;  $E_T(O-O\ O2p.O2p) = -1.65376\ eV$ ;

$$E_T(N-N N2p.N2p) = -1.44915 eV$$
;  $E_T(N-O N2p.O2p) = -1.44915 eV$ ;

$$E_r(F-F F2p.F2p) = -1.44915 \ eV; E_r(Cl-Cl Cl3p.Cl3p) = -0.92918 \ eV;$$

$$E_T(Br - Br Br 4p.Br 4p) = -0.92918 \ eV$$
;  $E_T(I - I I5p.I5p) = -0.36229 \ eV$ ;

$$E_T(C-F\ C2sp^3.F2p) = -1.85836\ eV$$
;  $E_T(C-Cl\ C2sp^3.Cl3p) = -0.92918\ eV$ ;

20 
$$E_T(C-Br\ C2sp^3.Br4p) = -0.72457\ eV$$
;  $E_T(C-I\ C2sp^3.I5p) = -0.36228\ eV$ , and

 $E_T(O-Cl\ O2p.Cl3p) = -0.92918\ eV$ , wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to + 10%, if desired.

- 379. The system of claim 366, wherein in the case that the terminal bond is X X where X is a halogen atom,  $c_1$  is one, and  $c_2$  is the average (Eq. (15.93)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.62-15.63) where
- 5  $E_{Coulomb}$  (MO.atom, msp<sup>3</sup>) is determined using Eq. (15.32) and  $E_{Coulomb}$  (MO.atom, msp<sup>3</sup>) = 13.605804 eV for X = I.
  - 380. The system of claim 379, wherein the factor  $C_1$  of Eq. (15.90) is one for all halogen atoms.

381. The system of claim 379, wherein the factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), wherein the calculated and measured values and constants recited in the equations herein

can be adjusted, for example, up to  $\pm$  10%, if desired.

- 382. The system of claim 379, wherein for each of the halogens, Cl, Br, and I,  $C_2$  is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with  $c_2$  (1) being that of the halogen given by Eq. (15.68) that matches the valence energy of X ( $E_1$ (valence)) to that of the  $C2sp^3$  HO ( $E_2$ (valence) = -14.63489 eV, Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2$ (2) = 0.91771, Eq. (13.430)), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.
- 25 383. The system of claim 382, wherein  $E_T(atom-atom, msp^3.AO)$  of Eq. (15.90) is the maximum for the participating atoms which is -1.44915~eV, -0.92918~eV, and -0.33582~eV for F, Cl, Br, and I, respectively, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

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- 979 The system of claim 366, wherein in the case that the terminal bond is C-X where 384. C is a carbon atom and X is a halogen atom, the factors  $c_1$  and  $c_2$  of Eq. (15.90) are one for all halogen atoms.
- The system of claim 384, wherein for X = F,  $c'_2$  is the average (Eq. (15.95)) of the 5 385. hybridization factors of the participating carbon and F atoms where  $c_2$  for carbon is given by Eq. (15.62) and  $c_2$  for fluorine matched to carbon is given by Eq. (15.70) with  $c_2(1)$  for the fluorine atom given by Eq. (15.68) that matches the valence energy of F  $(E_1(valence) = -17.42282 \ eV)$  to that of the  $C2sp^3$  HO  $(E_2(valence) = -14.63489 \ eV)$ ,
- Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2(2) = 0.91771$ , Eq. (13.430)), 10 wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.
- 386. The system of claim 385, wherein the factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude 15 of the Coulombic energy between the electron and proton of H given by Eq. (1.243), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.
- The system of claim 385, wherein for each of the other halogens, Cl, Br, and I,  $c'_2$ 20 387. is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom.
- 388. The system of claim 387, wherein the  $C_2$  of the terminal-atom bond matches that 25 used to determine the energies of the corresponding C-X-bond MO.
  - 389. The system of claim 388, wherein  $C_2$  is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with  $c_2(1)$  for the halogen atom given by Eq. (15.68) that matches the valence energy of X ( $E_1(valence)$ ) to that of the  $C2sp^3$  HO
- $(E_2(valence) = -14.63489 eV$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO 30

- $(c_2(2) = 0.91771$ , Eq. (13.430)), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.
- 5 390. The system of claim 385, wherein  $E_T(atom-atom, msp^3.AO)$  of Eq. (15.90) is the maximum for the participating atoms which is -1.85836~eV, -0.92918~eV, -0.72457~eV, and -0.33582~eV for F, Cl, Br, and I, respectively, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

- 391. The system of claim 385, wherein in the case that the terminal bond is H X corresponding to the angle of the atoms HCX where C is a carbon atom and X is a halogen atom, the factors  $c_1$  and  $c_2$  of Eq. (15.90) are 0.75 for all halogen atoms.
- 15 392. The system of claim 385, wherein for X = F,  $c_2$  is given by Eq. (15.69) with  $c_2$  of the participating carbon and F atoms given by Eq. (15.62) and Eq. (15.65), respectively.
- 393. The system of claim 392, wherein the factor C<sub>2</sub> of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude
  20 of the Coulombic energy between the electron and proton of H given by Eq. (1.243), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.
- 394. The system of claim 393, wherein for each of the other halogens, Cl, Br, and I,  $c_2'$  is also given by Eq. (15.69) with  $c_2$  of the participating carbon given by Eq. (15.62) and  $c_2$  of the participating X atom given by  $c_2 = 0.91771$  (Eq. (13.430)) since the X atom is energy matched to the  $C2sp^3$  HO.
- 395. The system of claim 394, wherein  $C_2$  is given by Eq. (15.65) for the corresponding atom X where  $C_2$  matches the energy of the atom X to that of H.

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The system of claim 366, wherein the distance between the two atoms A and B of 396. the general molecular group ACB when the total energy of the corresponding A-B MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^2 + s_2^2 - 2s_1 s_2 \cos ine \theta = s_3^2$$
 (15.96).

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The system of claim 396, wherein with  $s_1 = 2c'_{C-A}$ , the internuclear distance of the 397. C-A bond,  $s_2=2c'_{C-B}$ , the internuclear distance of each C-B bond, and  $s_3=2c'_{A-B}$ , the internuclear distance of the two terminal atoms, the bond angle  $\theta_{\angle ACB}$  between the C-A and C-B bonds is given by

10 
$$(2c'_{C-A})^{2} + (2c'_{C-B})^{2} - 2(2c'_{C-A})(2c'_{C-B})\operatorname{cosine}\theta = (2c'_{A-B})^{2}$$

$$\theta_{\angle ACB} = \cos^{-1}\left(\frac{(2c'_{C-A})^{2} + (2c'_{C-B})^{2} - (2c'_{A-B})^{2}}{2(2c'_{C-A})(2c'_{C-B})}\right)$$
(15.98).

The system of claim 397, wherein the structure  $C_bC_a(O_a)O_b$  wherein  $C_a$  is bound to  $C_b$ ,  $O_a$ , and  $O_b$ , the three bonds are coplanar and two of the angles are known, say  $\theta_1$ and  $\theta_2$ , then the third  $\theta_3$  can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \qquad (15.99)$$

The system of claim 397, wherein in the general case that two of the three coplanar 399. bonds are equivalent and one of the angles is known, say  $\theta_1$ , then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{(360 - \theta_1)}{2}$$
 (15.100).

- 400. The system of claim 1, wherein in the general case where the group comprises three A-B bonds having B as the central atom at the apex of a pyramidal structure formed by the three bonds with the A atoms at the base in the xy-plane. 25
  - 401. The system of claim 400, wherein the  $C_{3}$ , axis centered on B is defined as the vertical or z-axis, and any two A-B bonds form an isosceles triangle, and the angle of

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the bonds and the distances from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416):

the distance  $d_{origin-B}$  from the origin to the nucleus of a terminal B atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60^{\circ}} \qquad (15.101)$$

5 the height along the z-axis from the origin to the A nucleus  $d_{height}$  is given by

$$d_{height} = \sqrt{(2c'_{A-B})^2 - (d_{origin-B})^2}$$
, and (15.102)

the angle  $\theta_{\star}$  of each A-B bond from the z-axis is given by

$$\theta_{v} = \tan^{-1} \left( \frac{d_{origin-B}}{d_{height}} \right) \quad (15.103).$$

10 402. The system of claim 401, wherein in the case where the central atom B is further bound to a fourth atom C and the B-C bond is along the z-axis. Then, the bond  $\theta_{\angle ABC}$  given by Eq. (14.206) is

$$\theta_{\angle ABC} = 180 - \theta_{\nu} \qquad (15.104).$$

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- 403. The system of claim 400, wherein in the plane defined by a general ACA MO comprising a linear combination of two C-A-bond MOs where C is the central atom, the dihedral angle  $\theta_{\angle BC/ACA}$  between the ACA-plane and a line defined by a third bond with C, specifically that corresponding to a C-B-bond MO, is calculated from the bond angle  $\theta_{\angle ACA}$  and the distances between the A, B, and C atoms.
- 404. The system of claim 403, wherein the distance  $d_1$  along the bisector of  $\theta_{\angle ACA}$  from C to the internuclear-distance line between A and A,  $2c'_{A-A}$ , is given by

$$d_1 = 2c'_{C-A} \cos \frac{\theta_{\angle ACA}}{2}$$
 (15.105)

- 25 where  $2c'_{C-A}$  is the internuclear distance between A and C.
  - 405. The system of claim 404, wherein the atoms A, A, and B define the base of a pyramid.

406. The system of claim 405, wherein the pyramidal angle  $\theta_{\angle ABA}$  can be solved from the internuclear distances between A and A,  $2c'_{A-A}$ , and between A and B,  $2c'_{A-B}$ , using the law of cosines (Eq. (15.98)):

5 
$$\theta_{\angle ABA} = \cos^{-1}\left(\frac{\left(2c'_{A-B}\right)^2 + \left(2c'_{A-B}\right)^2 - \left(2c'_{A-A}\right)^2}{2\left(2c'_{A-B}\right)\left(2c'_{A-B}\right)}\right) \quad (15.106).$$

407. The system of claim 406, wherein the distance  $d_2$  along the bisector of  $\theta_{\angle ABA}$  from B to the internuclear-distance line  $2c'_{A-A}$ , is given by

$$d_2 = 2c'_{A-B} \cos \frac{\theta_{\angle ABA}}{2}$$
 (15.107).

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408. The system of claim 407, wherein the lengths  $d_1$ ,  $d_2$ , and  $2c'_{C-B}$  define a triangle wherein the angle between  $d_1$  and the internuclear distance between B and C,  $2c'_{C-B}$ , is the dihedral angle  $\theta_{CBC/ACA}$  that can be solved using the law of cosines (Eq. (15.98)):

$$\theta_{\angle BC/ACA} = \cos^{-1} \left( \frac{d_1^2 + (2c'_{C-B})^2 - d_2^2}{2d_1(2c'_{B-C})} \right)$$
 (15.108).

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409. The system of claim 1, wherein the specie are solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies where linearly added to achieve the molecular solutions, each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination, each functional group element was solved using the atomic orbital and hybrid orbital spherical orbitsphere solutions bridged by molecular orbitals comprised of the H<sub>2</sub>-type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section, the energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs, the energy
25 E<sub>mag</sub> (e.g. given by Eq. (15.58)) for a C2sp³ HO and Eq.(15.59) for an O2p AO) was subtracted for each set of unpaired electrons created by bond breakage.

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- 410. They system of claim 409, wherein the bond energy is not equal to the component energy of each bond as it exists in the specie, although, they are close.
- 411. The system of claim 409, wherein the total energy of each group is its contribution to the total energy of the specie as a whole.
  - 412. The system of claim 409, wherein the determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage.
- 413. The system of claim 409, wherein the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group, which will effect the functional-group energy, however because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they are neglected.
- 414. The system of claim 409, wherein the energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and  $E(C, 2sp^3) = -14.63489 \, eV$  (Eq. (13.428)).
  - 415. The system of claim 409, wherein the intercept angles are determined from Eqs. (15.71-15.78) using the final radius of the HO of each atom.

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- 416. The system of claim 409, wherein a final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined.
- 30 417. The system of claim 416, wherein the final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the corresponding final radius.

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418. The system of claim 417, wherein the radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell.

- 419. The system of claim 416, wherein the donation of electron density to the AOs and HOs reduces the energy.
- 420. The system of claim 419, wherein the donation of the electron density to the MO's at each AO or HO is that which causes the resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.
- 421. The system of claim 1, wherein the molecular solutions are used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation.
  - 422. The system of claim 1, wherein the new stable compositions of matter are predicted as well as the structures of combinatorial chemistry reactions.
- 20 423. The system of claim 1, wherein pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the specie to be identified from the common spatial charge-density functions of a series of active species.
- 25 424. The system of claim 1, wherein novel drugs are designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the drug.
- 425. The system of claim 1, wherein to calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given specie are used to calculate the fields, and from the fields, the interactions between groups of the same specie or between groups on different species are calculated wherein the interactions are distance and relative orientation dependent.

- 426. The system of claim 425, the fields and interactions can be determined using a finiteelement-analysis approach of Maxwell's equations.
- 427. The system of claim 1, wherein in the case where three sets of C = C-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons, and each bond comprises a linear combination of two MOs wherein each comprises two C2sp³ HOs and 75% of a H<sub>2</sub>-type ellipsoidal MO divided between the C2sp³ HOs:

$$\begin{pmatrix}
3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C=C) - \text{ ethylene - type - bond MO} \\
\rightarrow 6(C=C) - \text{ bond MO of benzene}
\end{pmatrix} (15.142).$$

- 428. The system of claim 427, wherein the linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution per bond from each  $C2sp^3$  HO to the C=C-bond MO to achieve an energy minimum.
- 15 429. The system of claim 427, wherein the dimensional parameters of each bond C = C-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the C = C-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

- 430. The system of claim 427, wherein hybridization with 25% electron donation to each C = C-bond gives rise to the  $C_{benzens} 2sp^3$  HO-shell Coulombic energy  $E_{Coulomb} \left( C_{benzene}, 2sp^3 \right)$  given by Eq. (14.245).
- 25 431. The system of claim 427, wherein to meet the equipotential condition of the union of the six  $C2sp^3$  HOs,  $c_2$  and  $c_3$  of Eq. (15.42) for the aromatic  $c_3$  the six  $c_3$  hos,  $c_4$  and  $c_5$  of Eq. (15.42) for the aromatic  $c_4$  bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of  $c_4$  because,  $c_5$  (Eq.

(14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2$$
 (benzeneC2sp³HO)= $c_2$  (benzeneC2sp³HO)= $\frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252$  (15.143)

wherein the calculated and measured values and constants recited in the equations herein can  $\frac{1}{2}$  be adjusted, for example, up to  $\frac{1}{2}$  10%, if desired.

432. The system of claim 427, wherein the energies of each C=C bond of benzene are determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene.

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- 433. The system of claim 427, wherein ethylene serves as a basis element for the C=C bonding of benzene wherein each of the six C=C bonds of benzene comprises (0.75)(4)=3 electrons according to Eq. (15.142).
- 15 434. The system of claim 427, wherein the total energy of the bonds of the eighteen electrons of the C=C bonds of benzene,  $E_T\left(C_6H_6,C=C\right)$ , is given by (6)(0.75) times  $E_{T+asc}\left(C=C\right)$  (Eq. (14.492)), the total energy of the C=C-bond MO of benzene including the Doppler term, minus eighteen times  $E\left(C,2sp^3\right)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each C that forms the C=C bonds of bond order two.

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435. The system of claim 427, wherein the total energy of the six C = C bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$E_{T}\left(C_{6}H_{6},C=C\right) = (6)(0.75)E_{T+osc}\left(C=C\right) - (6)(3)E\left(C,2sp^{3}\right)$$

$$= (6)(0.75)\left(-66.05796 \ eV\right) - 18\left(-14.63489 \ eV\right) (15.144)$$

$$= -297.26081 \ eV - \left(-263.42798 \ eV\right)$$

$$= -33.83284 \ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

436. The system of claim 427, wherein the results of benzene can be generalized to the class of aromatic and heterocyclic compounds.  $E_{h\nu}$  of an aromatic bond is given by  $E_T(H_2)$  (Eqs. (11.212) and (14.486)), the maximum total energy of each  $H_2$ -type MO such that

$$\overline{E}_{ox} = \eta_1 \left( \overline{E}_D + \overline{E}_{Kvib} \right) = \eta_1 \left( -31.63536831 \ eV \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.145)

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

437. The system of claim 435, wherein the factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule ( $C_6H_6$ ) section modifies Eqs. (15.52-15.56).

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438. The system of claim 437, wherein the multiplication of the total energy given by Eq. (15.55) by  $f_1 = 0.75$  with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

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$$E_{T}(Group) = f_{1} \begin{cases} E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) \\ -31.63536831\ eV \\ \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{m_{e}}} + n_{1}\overline{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} \end{cases}$$
(15.146)

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

439. The system of claim 427, wherein the total bond energy of the aromatic group  $E_D \text{ (Group)} \text{ is the negative difference of the total energy of the group (Eq. (15.146)) and the}$ 

total energy of the starting species given by the sum of  $c_4 E_{tnitial} (c_4 AO/HO)$  and  $c_5 E_{tnitial} (c_5 AO/HO)$ :

$$E_{D}(Group) = -\left( f_{1} \left( E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) \right) - 31.63536831\ eV \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}} - \frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}} - \frac{8\pi\mu_{o}\mu_{B}^{2}}{m_{e}c^{2}} + n_{1}\overline{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} \right) - \left( c_{4}E_{initial}(AO/HO) + c_{5}E_{initial}(c_{5}AO/HO) \right)$$

(15.147), wherein the calculated and measured values and constants recited in the 5 equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

- 440. The system of claim 427, wherein benzene is considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms, energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  are the same
- as those of the hydrogen carbide radical, except that  $E_T(C=C,2sp^3)=-1.13379~eV$  (Eq. (14.247)) is subtracted from  $E_T(CH)$  of Eq. (13.495) to match the energy of each C-H-bond MO to the decrease in the energy of the corresponding  $C2sp^3$  HO, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

- 441. The system of claim 440, wherein in the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with E<sub>T</sub> (atom atom, msp³.AO)=-1.13379 eV wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.
  - 442. The system of claim 440, wherein the total energy of the benzene C-H-bond MO,  $E_{T_{benzene}}(C-H)$ , given by Eq. (14.467) is the sum of  $0.5E_{T}(C=C,2sp^{3})$ , the energy change of each  $C2sp^{3}$  shell per single bond due to the decrease in radius with the

formation of the corresponding C=C-bond MO (Eq. (14.247)), and  $E_{T_{beauton}}$  (CH), the  $\sigma$  MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with  $f_1=1$  and  $E_T(atom-atom,msp^3.AO)=\frac{-1.13379\ eV}{2}$ , wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

- 443. The system of claim 442, wherein the energy contribution to the single aromatic CH bond is one half that of the C=C double bond contribution, which matches the energies
   of the CH and C=C aromatic groups, conserves the electron number with the equivalent charge density as that of s=1 in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule.
- - 445. The system of claim 444, wherein each of the C-H bonds of benzene comprises two electrons according to Eq. (14.439).
- 446. The system of claim 445, wherein from the energy of each C-H bond,  $-E_{D_{bonzero}}\binom{12}{CH}$  (Eq. (14.477)), the total energy of the twelve electrons of the six C-H bonds of benzene,  $E_T(C_6H_6,C-H)$ , given by Eq. (14.494) is  $E_T(C_6H_6,C-H) = (6)(-E_{D_{bonzero}}\binom{12}{CH}) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV}$
- 25 (15.148), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.

447. The system of claim 440, wherein the total bond dissociation energy of benzene,

$$E_D(C_6H_6)$$
, given by Eq. (14.495) is the negative sum of  $E_T(C_6H_6, C=C)$  (Eq.

(14.493)) and  $E_T(C_6H_6, C-H)$  (Eq. (14.494)):

$$E_{D}(C_{6}H_{6}) = -\left(E_{T}(C_{6}H_{6}, C = C) + E_{T}(C_{6}H_{6}, C - H)\right)$$

$$= -\left((-33.83284 \, eV) + (-23.42724 \, eV)\right)$$

$$= 57.2601 \, eV$$
(15.149)

- 5 wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to  $\pm$  10%, if desired.
  - 448. The system of claim 447, wherein using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147))
- reproduces the results for benzene given in the Benzene Molecule  $(C_6H_6)$  section as shown in Tables 15.214 and 15.216.
  - 449. A system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising:

processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie to produce at least one Maxwellian

20 solution; and

15

an output means for outputting the Maxwellian solution.

- 450. The system of claim 449, further comprising a data transfer system for inputting numerical data into or out of a computational components and storage components of the main system.
  - 451. The system of claim 449, further comprising a spreadsheet containing solutions of the bond parameters with output in a standard spreadsheet format.

- 452. The system of claim 451, further comprising a data-handling program to transfer data from the spreadsheets into the main program.
- 5 453. The system of claim 449, wherein output may be at least one of graphical, simulation, text, and numerical data.
- 454. The system of claim 453, wherein the output may be the calculation of at least one of:
  (1) a bond distance between two of the atoms; (2) a bond angle between three of the
  atoms; (3) a bond energy between two of the atoms; (4) orbital intercept distances and angles; and (5) charge-density functions of atomic, hybridized, and molecular orbitals, wherein the bond distance, bond angle, and bond energy are calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration
  - 455. The system of claim 449, wherein the charge, current, energy, and geometrical parameters are output to be inputs to other programs that can be used in further applications.

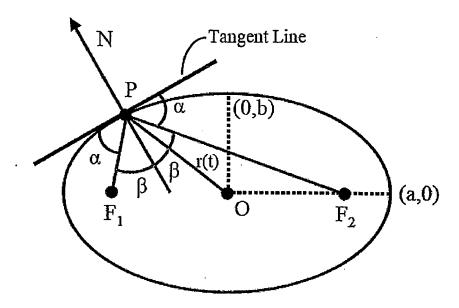
- 456. The system of claim 455, wherein the data of heats of formation can be input to another program to be used to predict stability (existence of compounds) equilibrium constants and to predict synthetic pathways.
- 25 457. The system of claim 456, wherein novel composition of matters can be discovered by calculating at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

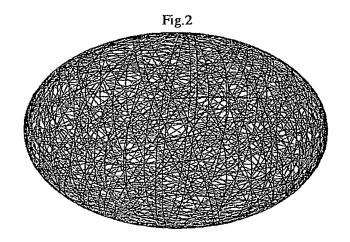
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- 458. The system of claim 456, wherein the charge and current density functions can be used to predict the electric and magnetic fields of the species to determine other properties due to the interaction of the fields between species.
- 5 459. The system of claim 458, wherein finite-element analysis is used to predict or calculate the interaction and resulting properties, such as the freezing point, boiling point, density, viscosity, and refractive index.
- 460. The system of claim 449, wherein the output data can be used to give thermodynamic, spectroscopic, and other properties, aid in drug design and other applications with or without direct visualization.
- 461. The system of claim 449, wherein the data can be input into other programs of the system, which calculate thermodynamic and other properties, or performs a simulation,
  such as a chemical reaction or molecular dynamics.
  - 462. A method of using any of the systems or compositions of matter of claims 1-461.
  - 463. A use of any system or composition of matter of claims 1-461.

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Fig.1





2/51 Fig.3

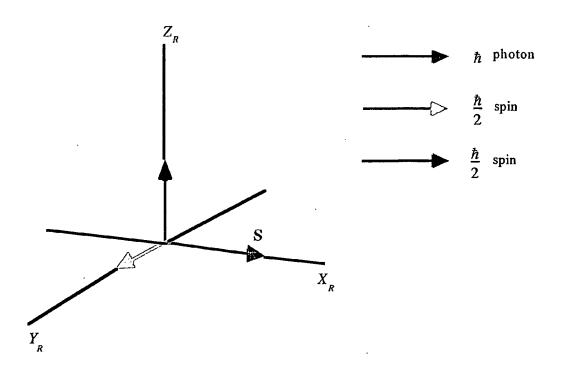
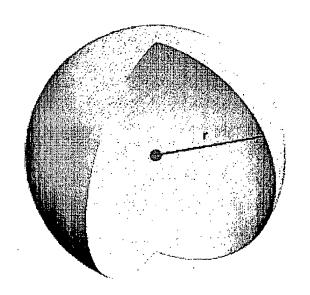
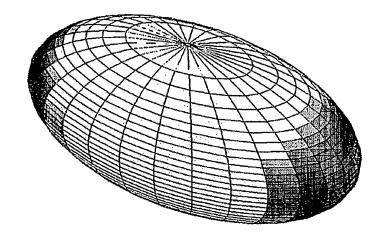


Fig.4



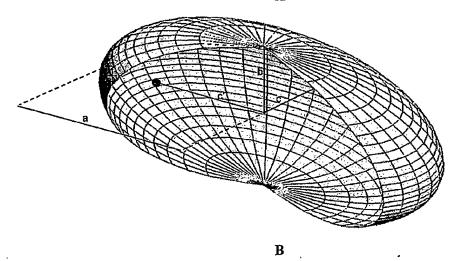
3/51

Fig.5

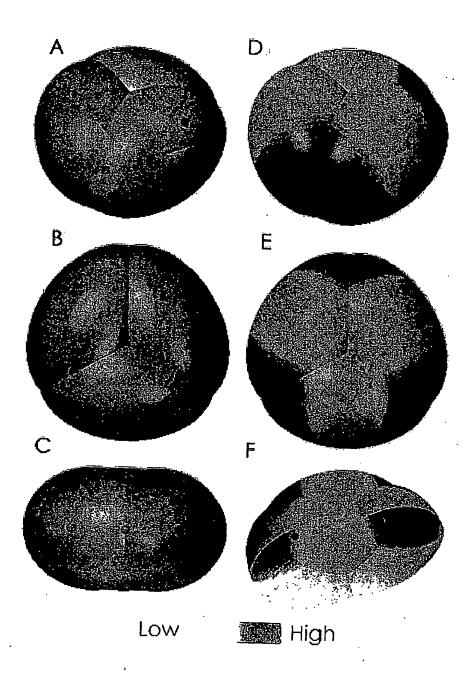




Increasing Electron Density



4/51 Fig. 6



5/51 Fig.7

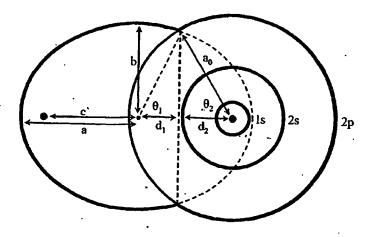
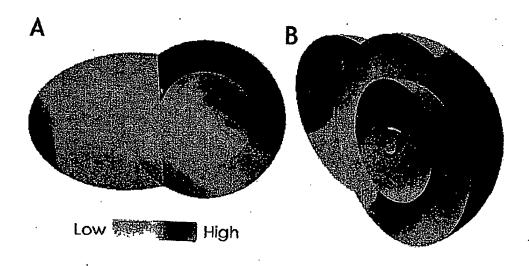


Fig.8



6/51 Fig.9

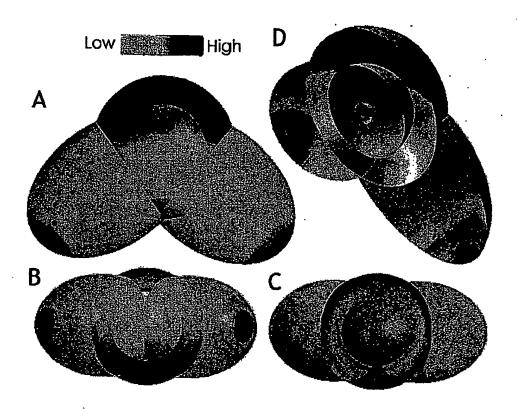
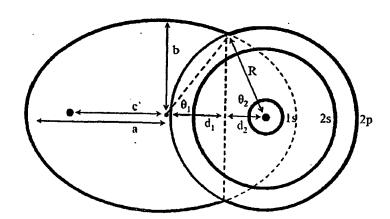


Fig. 10



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Fig.11

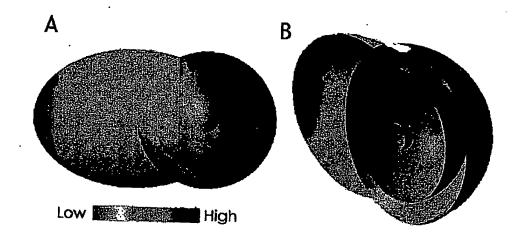
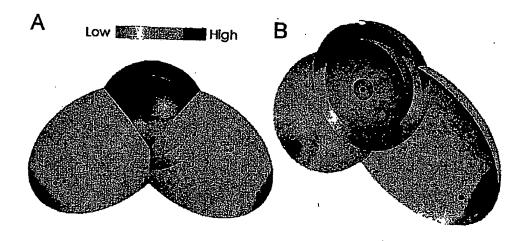
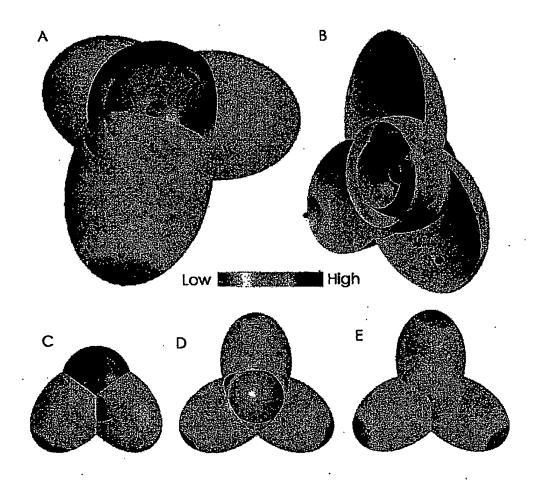


Fig.12



8/51 Fig.13



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9/51 Fig.14

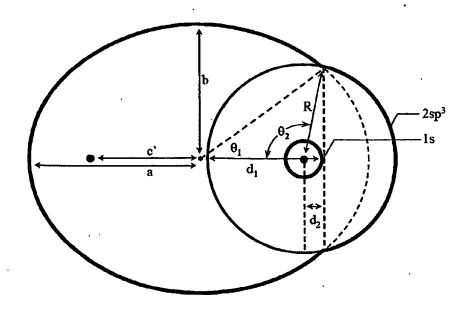
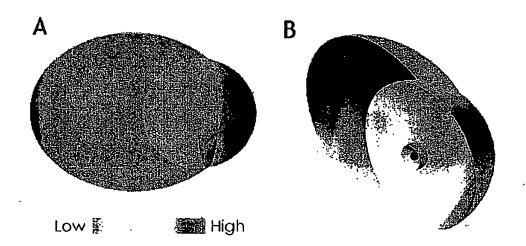


Fig.15



10/51 Fig.16

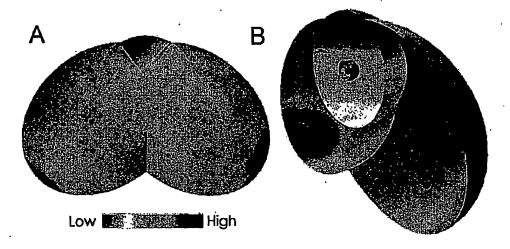
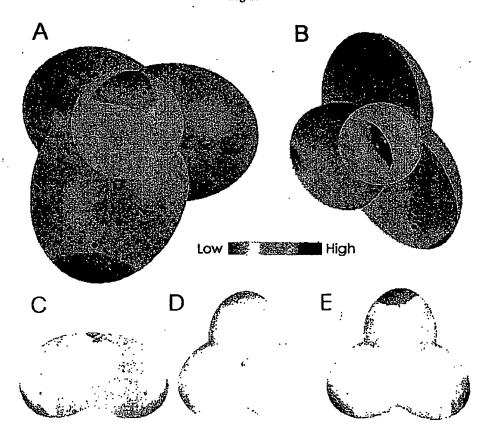
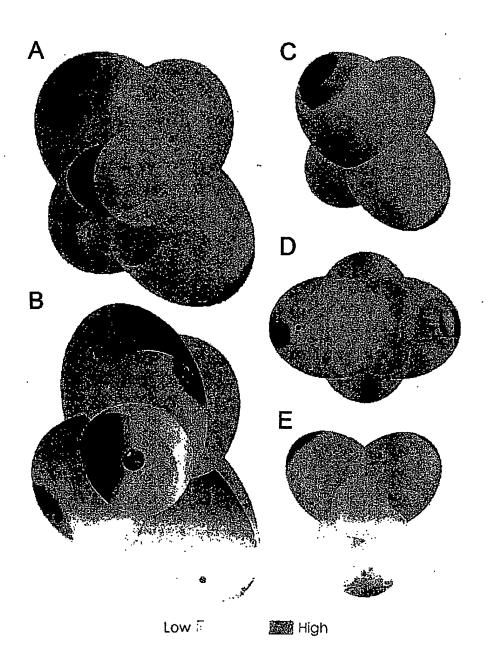


Fig.17



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Fig.18



12/51 Fig.19

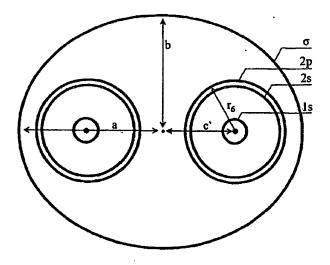
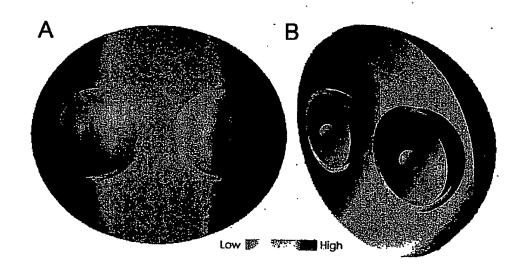


Fig.20



13/51 Fig.21

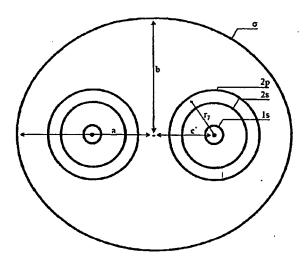
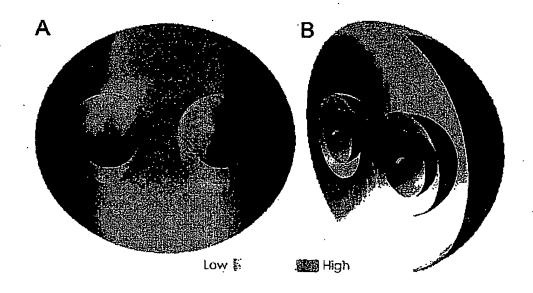


Fig.22



14/51 Fig.23

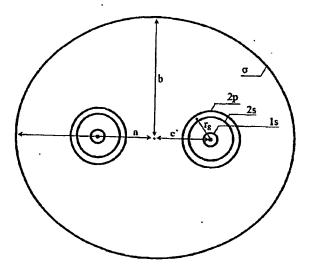
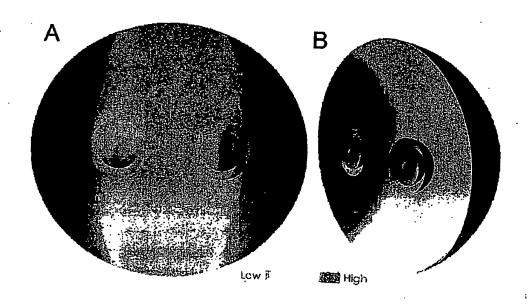


Fig.24



15/51 Fig.25

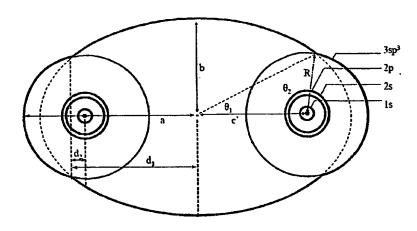
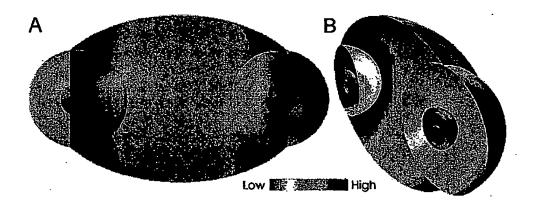


Fig.26



16/51 Fig.27

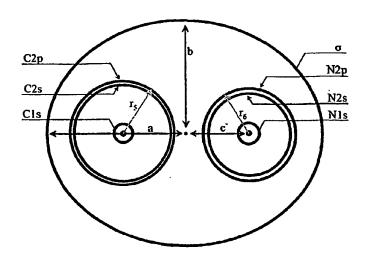
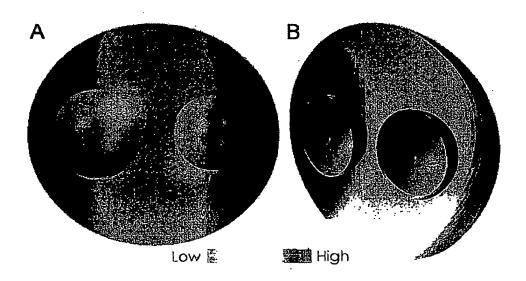


Fig.28



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17/51 Fig.29

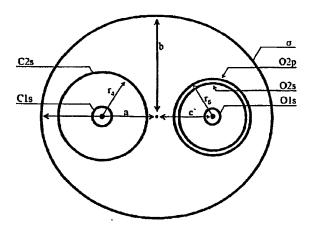
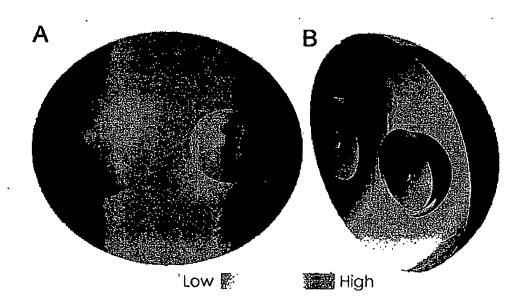


Fig.30



18/51 Fig.31

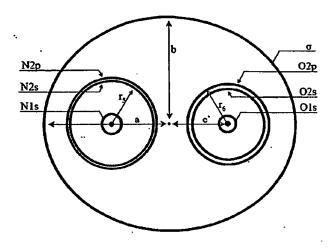
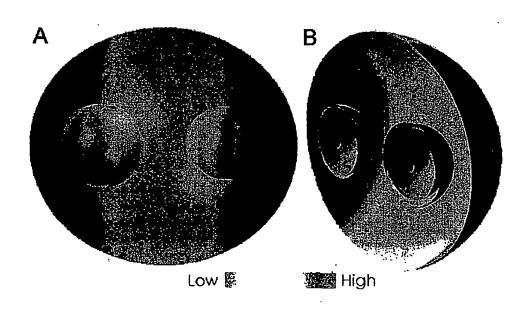


Fig.32



19/51 Fig.33

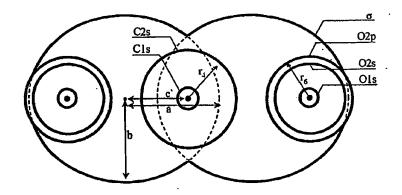
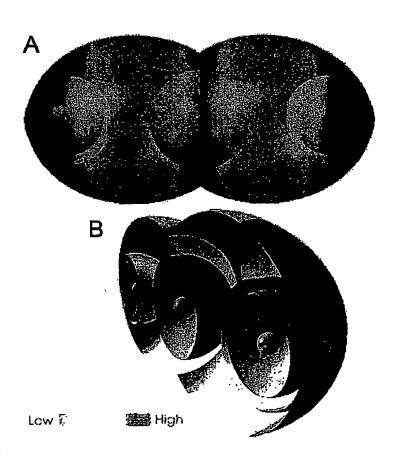


Fig.34



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Fig.35

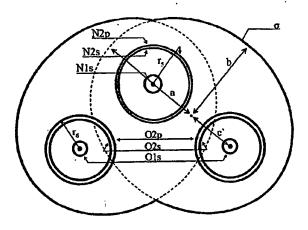
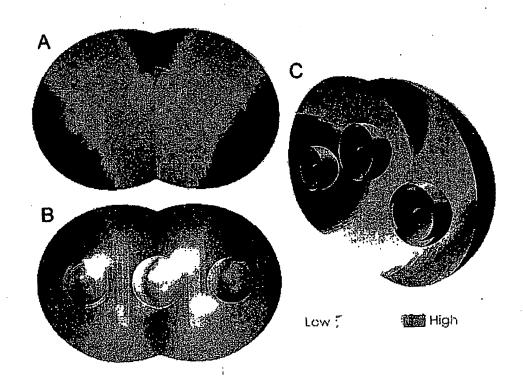


Fig.36



**21/51** Fig.37

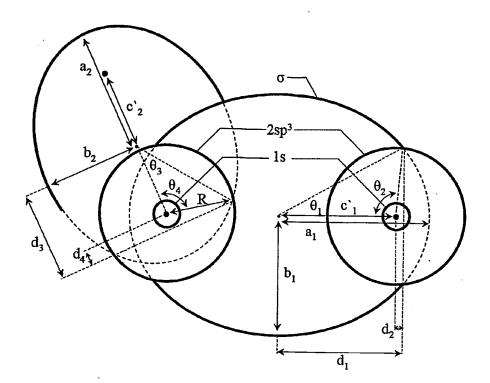
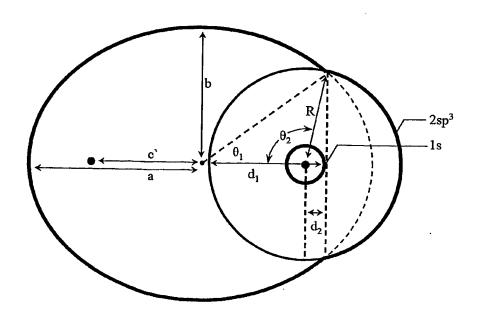
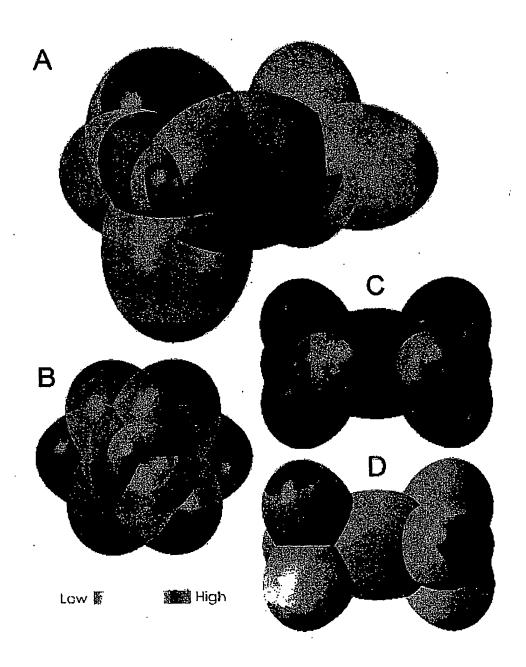


Fig.38



22/51 Fig.39



**23/51** Fig.40

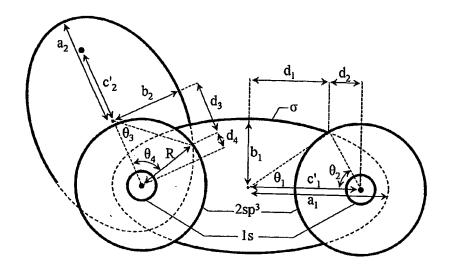
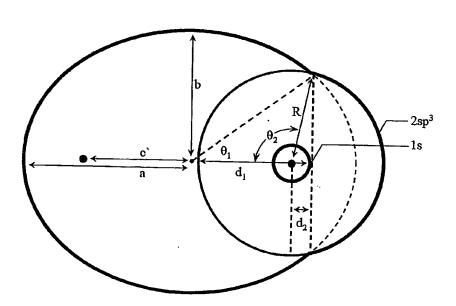
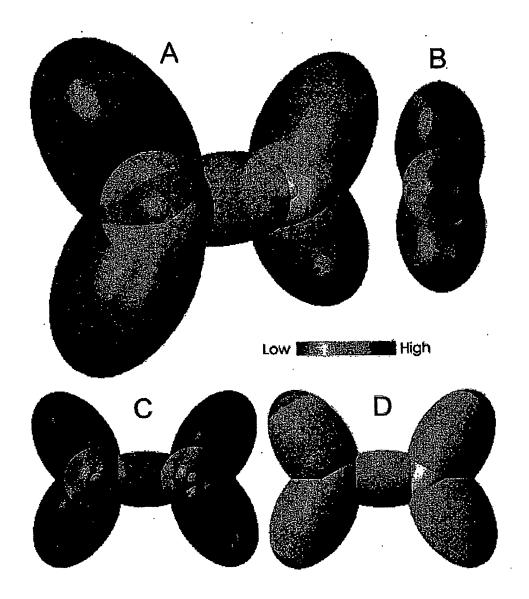


Fig.41



24/51 Fig.42



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25/51 Fig.43

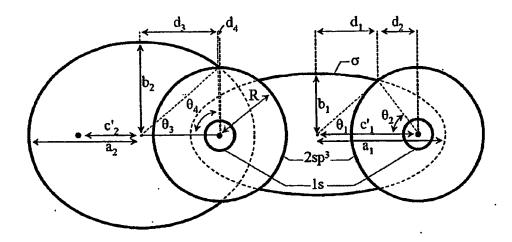
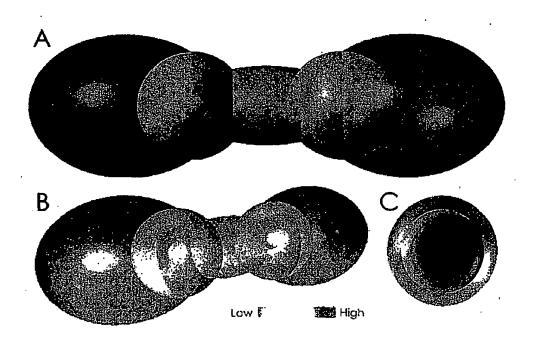


Fig.44



**26/51** Fig.45

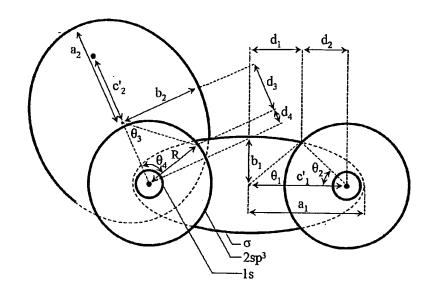
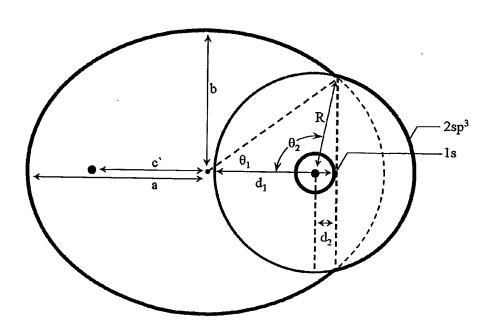
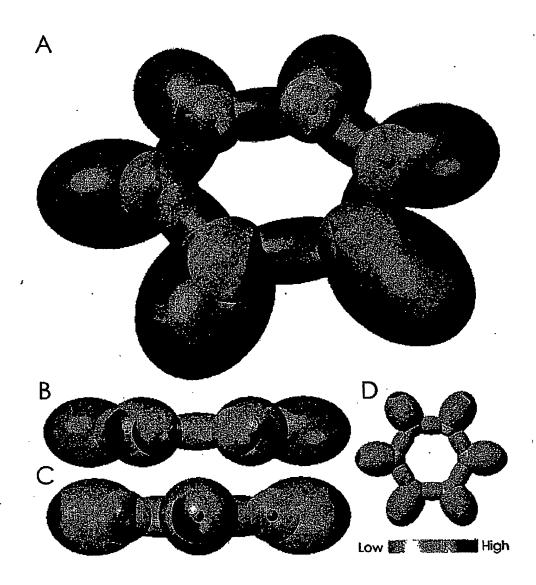


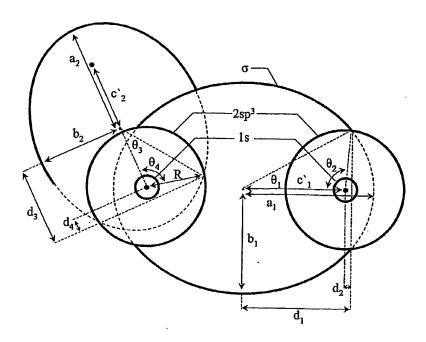
Fig.46



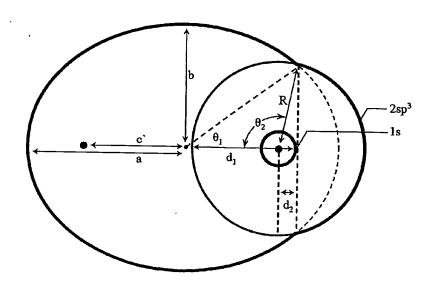
**27/51** Fig.47



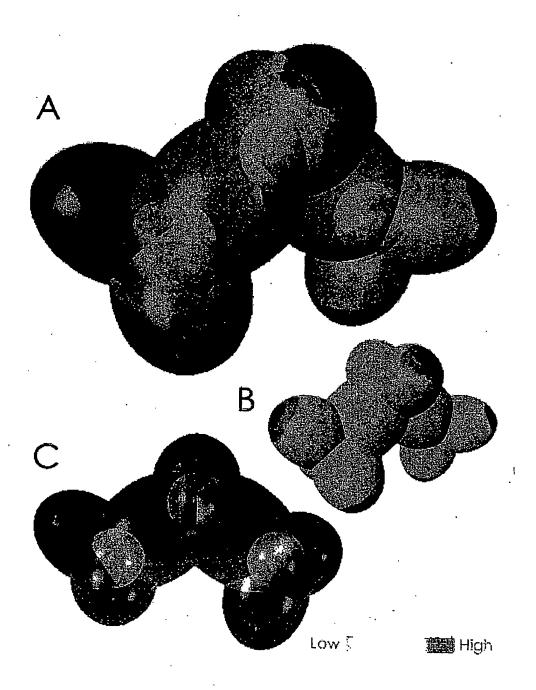
**28/51** Fig.48



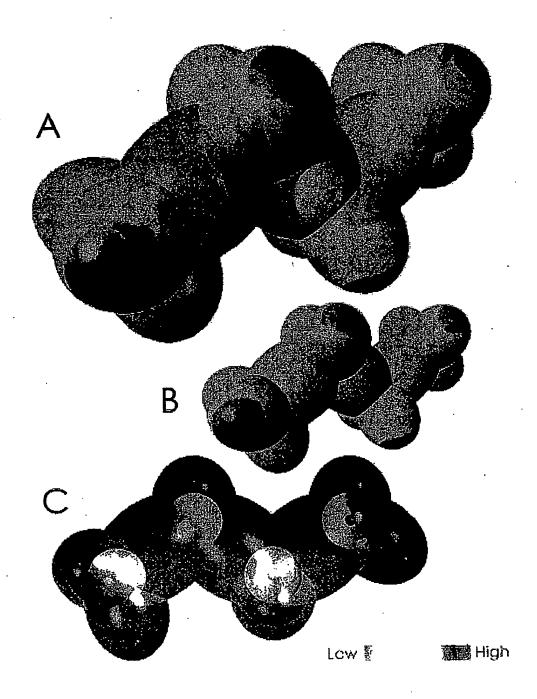
: Fig.49

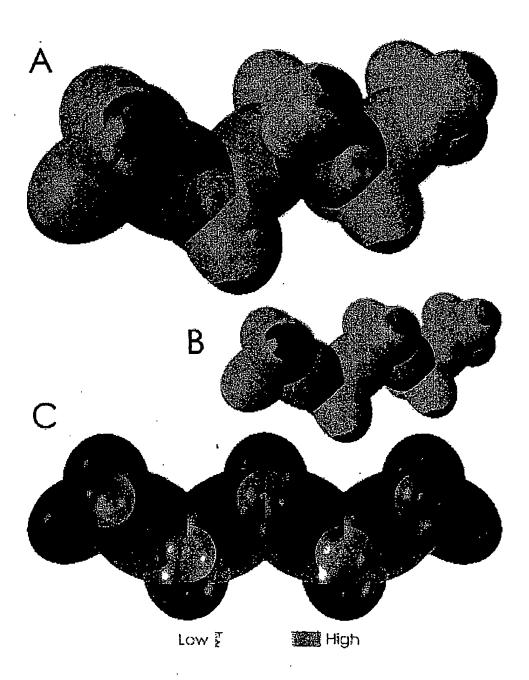


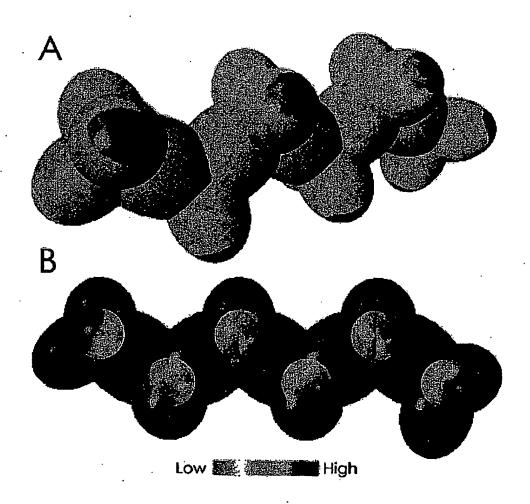
29/51 Fig.50



30/51 Fig.51

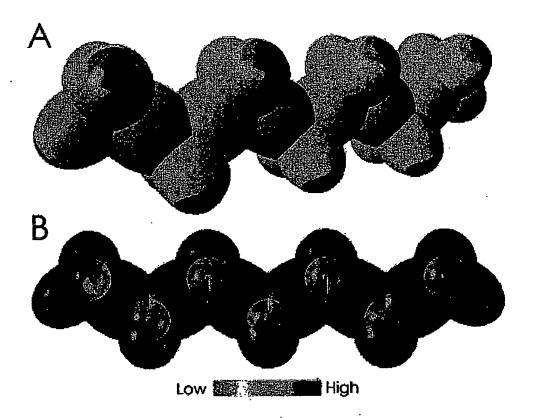






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34/51 Fig.55

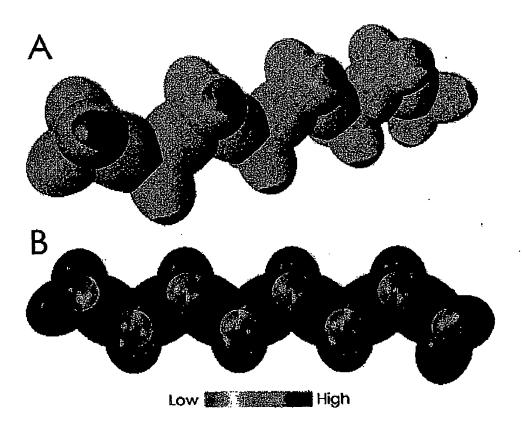
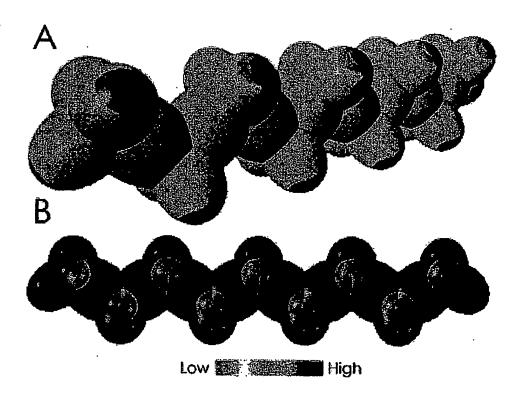
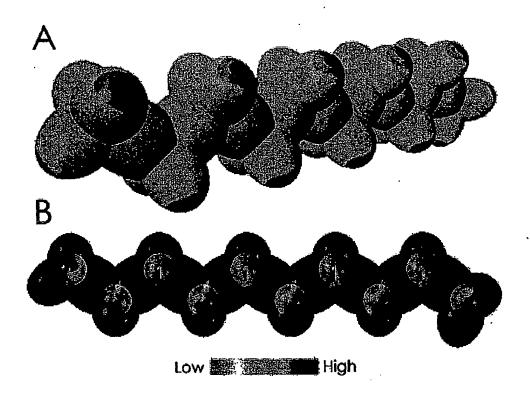
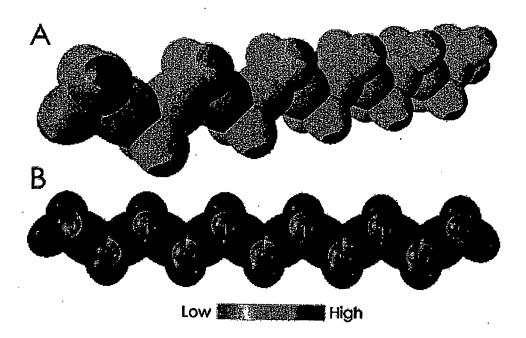


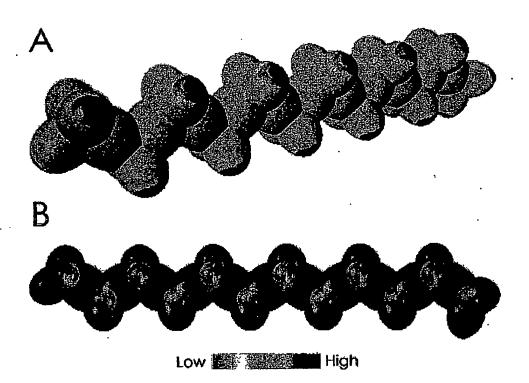
Fig.56







38/51 Fig.59



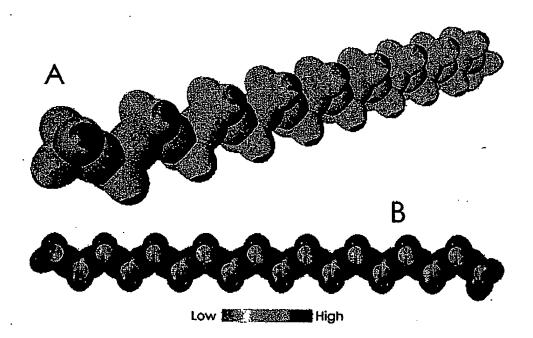


Fig. 61.A

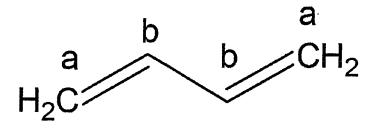


Fig. 61.B

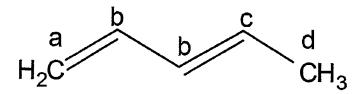
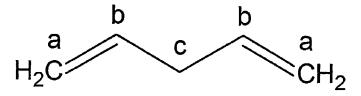


Fig. 61.C



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Fig. 61.D

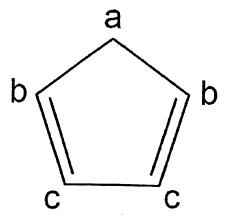
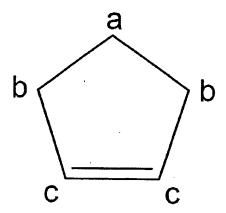


Fig. 61E



**42/51** Fig. 62

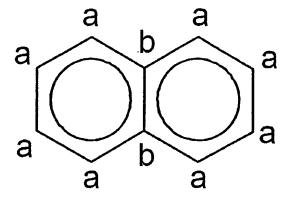


Fig. 63

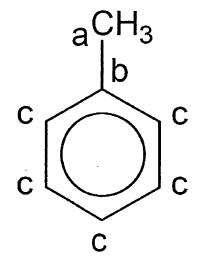
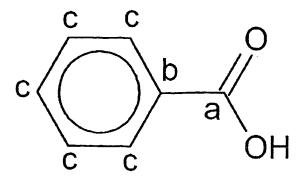


Fig. 64



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Fig. 65

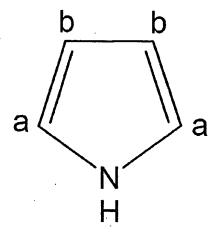


Fig. 66

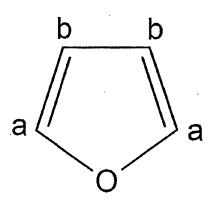


Fig. 67

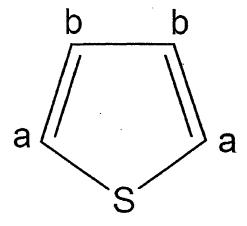


Fig. 68

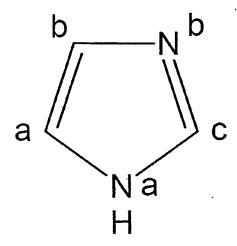


Fig. 69

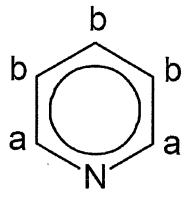
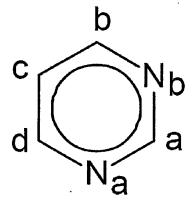


Fig. 70



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Fig. 71

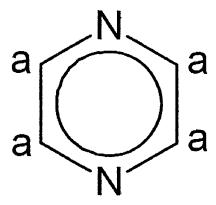


Fig.72

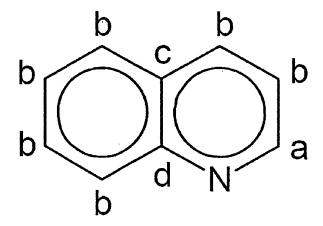


Fig. 73

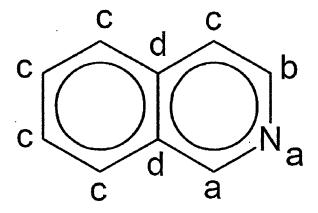
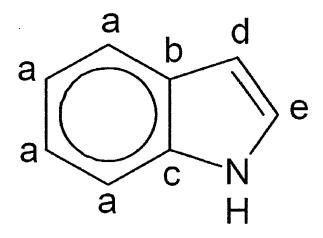
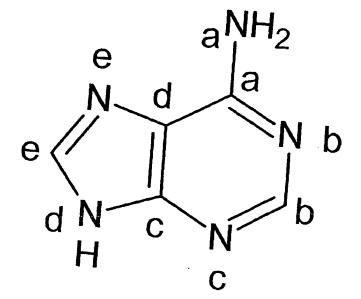
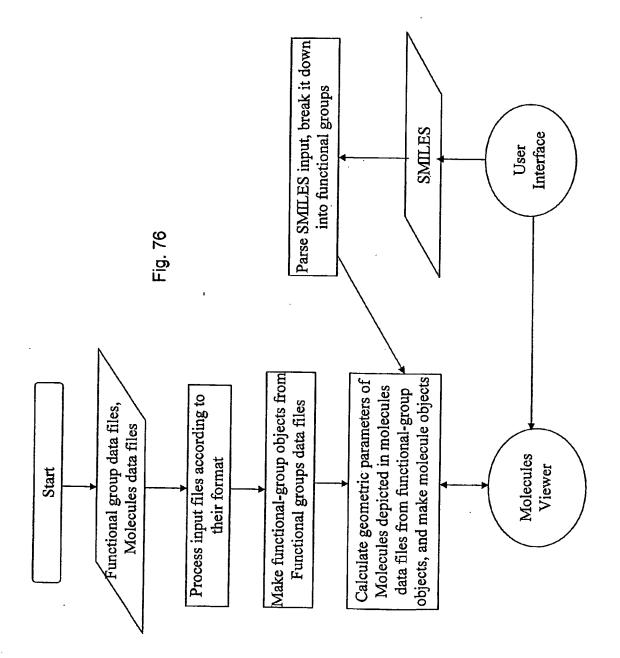


Fig. 74

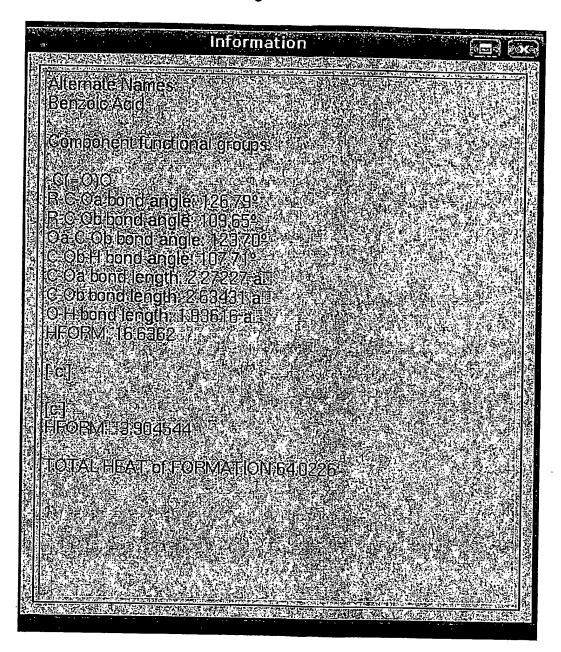


**48/51** Fig. 75

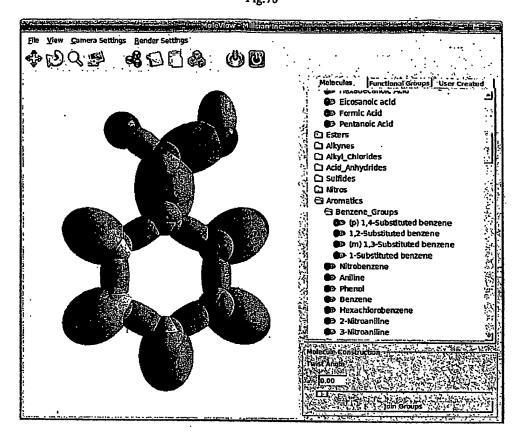




50/51 Fig. 77



51/51 · Fig.78



## **Section IV**

# ORGANIC MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

5 Organic molecules comprising an arbitrary number of atoms can be solved using the similar principles and procedures as those used to solve alkanes of arbitrary length. Alkanes can be considered to be comprised of the functional groups of  $CH_1$ ,  $CH_2$ , and C-C. These groups with the corresponding geometrical parameters and energies can be added as a linear sum to give the solution of any straight chain alkane as shown in the Continuous-Chain Alkanes 10 section. Similarly, the geometrical parameters and energies of all functional groups such as alkanes, branched alkanes, alkenes, branched alkenes, alkyles, alkyl fluorides, alkyl chlorides, alkyl bromides, alkyl iodides, alkene halides, primary alcohols, secondary alcohols, tertiary alcohols, ethers, primary amines, secondary amines, tertiary amines, aldehydes, ketones, carboxylic acids, carboxylic esters, amides, N-alkyl amides, N,N-dialkyl amides, 15 urea, acid halides, acid anhydrides, nitriles, thiols, sulfides, disulfides, sulfoxides, sulfones, sulfites, sulfates, nitro alkanes, nitrites, nitrates, conjugated polyenes, aromatics, heterocyclic aromatics, substituted aromatics, and others can be solved. The functional-group solutions can be made into a linear superposition and sum, respectively, to give the solution of any organic molecule. The solutions of the functional groups can be conveniently obtained by 20 using generalized forms of the geometrical and energy equations. The equations and sections that are referenced by not contained in this text refer to those sections and equations of the book by R. L. Mills entitled, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at 25 http://www.blacklightpower.com/bookdownload.shtml which is incorporated in its entirety by reference.

Consider the case wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. The force generalized constant k' of a

 $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \tag{15.1}$$

where  $C_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the molecule or molecular ion which is 0.75 (Eq. (13.59)) in the case of H bonding to a 5 central atom and 0.5 (Eq. (14.152)) otherwise, and  $C_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond. From Eqs. (13.58-13.63), the distance from the origin of the MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (15.2)

10 The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.3}$$

The length of the semiminor axis of the prolate spheroidal MO b = c is given by

$$b = \sqrt{a^2 - c'^2} \tag{15.4}$$

And, the eccentricity, e, is

$$e = \frac{c'}{a} \tag{15.5}$$

From Eqs. (11.207-11.212), the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_{e} = n_{1}c_{1}c_{2} \frac{-2e^{2}}{8\pi\varepsilon\sqrt{a^{2} - b^{2}}} \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}}$$
(15.6)

The potential energy of the two nuclei is

$$V_{p} = n_{1} \frac{e^{2}}{8\pi\varepsilon_{o} \sqrt{a^{2} - b^{2}}}$$
 (15.7)

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(15.8)

And, the energy,  $V_m$ , of the magnetic force between the electrons is

$$V_{m} = n_{1}c_{1}c_{2}\frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}}\ln\frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}$$
(15.9)

The total energy of the  $H_2$ -type prolate spheroidal MO,  $E_T(H_1MO)$ , is given by the sum of the energy terms:

$$E_{r}(\mu_{2}MO) = V_{r} + T + V_{m} + V_{n}$$
 (15.10)

$$E_{T}(\mu_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[ c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right) \ln\frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}} - 1 \right]$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[ c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right) \ln\frac{a+c'}{a-c'} - 1 \right]$$
(15.11)

5

25

where  $n_i$  is the number of equivalent bonds of the MO and applies in the case of functional groups. In the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor. It is 1 for a single bond, 4 for an independent double bond as in the case of the CO<sub>2</sub> and NO<sub>2</sub> molecules, and 9 for an 10 independent triplet bond. Then, the kinetic energy term is multiplied by  $c'_{BO}$  which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond.  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of an MO which is 0.75 (Eqs. (13.67-13.73)) in the case of H bonding to an unhybridized central atom and 1 otherwise, and  $c_2$  is the factor that results in an equipotential energy match of the participating the MO and the at least two atomic orbitals 15 of the chemical bond. Specifically, to meet the equipotential condition and energy matching conditions for the union of the  $H_2$ -type-ellipsoidal-MO and the HOs or AOs of the bonding atoms, the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO may given by (i) one, (ii) the ratio of the Coulombic or valence energy of the AO or HO of at least one atom of the bond and 13.605804 eV, the Coulombic energy between the electron and proton of H, (iii) the ratio of 20 the valence energy of the AO or HO of one atom and the Coulombic energy of another, (iv) the ratio of the valence energies of the AOs or HOs of two atoms, (v) the ratio of two  $c_2$ factors corresponding to any of cases (ii)-(iv), and (vi) the product of two different  $c_2$  factors corresponding to any of the cases (i)-(v). Specific examples of the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO given in previous sections are

0.936127, the ratio of the ionization energy of N 14.53414 eV and 13.605804 eV, the Coulombic energy between the electron and proton of H;

$$448$$

$$0.91771, \text{ the ratio of } 14.82575 \ eV, -E_{Coulomb}(C, 2sp^3), \text{ and } 13.605804 \ eV;$$

$$0.87495, \text{ the ratio of } 15.55033 \ eV, -E_{Coulomb}(C_{ethane}, 2sp^3), \text{ and } 13.605804 \ eV;$$

$$0.85252, \text{ the ratio of } 15.95955 \ eV, -E_{Coulomb}(C_{ethylene}, 2sp^3), \text{ and } 13.605804 \ eV;$$

$$0.85252, \text{ the ratio of } 15.95955 \ eV, -E_{Coulomb}(C_{benzene}, 2sp^3), \text{ and } 13.605804 \ eV, \text{ and}$$

$$0.86359, \text{ the ratio of } 15.55033 \ eV, -E_{Coulomb}(C_{alkane}, 2sp^3), \text{ and } 13.605804 \ eV.$$

In the generalization of the hybridization of at least two atomic-orbital shells to form a shell of hybrid orbitals, the hybridized shell comprises a linear combination of the electrons of the atomic-orbital shells. The radius of the hybridized shell is calculated from the total Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and that the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons. The total energy  $E_T$  (atom,  $msp^3$ ) (m is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one AO shell.

15 
$$E_T(atom, msp^3) = -\sum_{m=1}^{n} IP_m$$
 (15.12)

where  $IP_m$  is the *m*th ionization energy (positive) of the atom. The radius  $r_{msp}$ , of the hybridized shell is given by:

$$r_{msp^3} = \sum_{q=Z-n}^{Z-1} \frac{-(Z-q)e^2}{8\pi\varepsilon_0 E_T \left(atom, msp^3\right)}$$
(15.13)

Then, the Coulombic energy  $E_{Coulomb}$  (atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> 20 shell is given by

$$E_{Coulomb}\left(atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp}},$$
(15.14)

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius r of the AO electron:

25 
$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3} = \frac{8\pi\mu_o \mu_B^2}{r^3}$$
 (15.15)

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Then, the energy  $E(atom, msp^3)$  of the outer electron of the  $atom msp^3$  shell is given by the sum of  $E_{Coulomb}(atom, msp^3)$  and E(magnetic):

$$E(atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r^{3}}$$
(15.16)

Consider next that the at least two atomic orbitals hybridize as a linear combination of 5 electrons at the same energy in order to achieve a bond at an energy minimum with another atomic orbital or hybridized orbital. As a further generalization of the basis of the stability of the MO, the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. In this case, the total energy of the 10 hybridized orbitals is given by the sum of  $E(atom, msp^3)$  and the next energies of successive ions of the atom over the n electrons comprising the total electrons of the at least two initial AO shells. Here,  $E(atom, msp^3)$  is the sum of the first ionization energy of the atom and the hybridization energy. An example of  $E(atom, msp^3)$  for  $E(C, 2sp^3)$  is given in Eq. (14.503) where the sum of the negative of the first ionization energy of C, -11.27671 eV, plus the 15 hybridization energy to form the  $C2sp^3$  shell given by Eq. (14.146) is  $E(C, 2sp^3) = -14.63489 eV$ .

Thus, the sharing of electrons between two  $atom msp^3$  HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each  $atom msp^3$  HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond. In each case, the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons plus the hybridization energy. The total energy  $E_T(mol.atom, msp^3)$  (m is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:

$$E_{T}\left(mol.atom, msp^{3}\right) = E\left(atom, msp^{3}\right) - \sum_{m=2}^{n} IP_{m}$$
(15.17)

where  $IP_m$  is the *m*th ionization energy (positive) of the atom and the sum of  $-IP_1$  plus the hybridization energy is  $E(atom, msp^3)$ . Thus, the radius  $r_{msp}$ , of the hybridized shell is given by:

$$r_{msp^3} = \left(\sum_{q=Z-n}^{Z-1} (Z-q) - s\left(0.25\right)\right) \frac{-e^2}{8\pi\varepsilon_0 E_T\left(mol.atom, msp^3\right)}$$
(15.18)

where s = 1, 2, 3 for a single, double, and triple bond, respectively. The Coulombic energy  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> shell is given by

$$E_{Coulomb}\left(mol.atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}}$$
(15.19)

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired 10 in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius r of the AO electron given by Eq. (15.15). Then, the energy  $E(mol.atom, msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by the sum of  $E_{Coulomb}$  ( $mol.atom, msp^3$ ) and E(magnetic):

$$E(mol.atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{men^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r^{3}}$$
(15.20)

15  $E_r$  (atom – atom,  $msp^3$ ), the energy change of each atom  $msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between E (mol.atom,  $msp^3$ ) and E (atom,  $msp^3$ ):

$$E_T(atom-atom, msp^3) = E(mol.atom, msp^3) - E(atom, msp^3)$$
 (15.21)

As examples from prior sections,  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) is one of:

20 
$$E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$$
,  $E_{Coulomb}\left(C_{ethane}, 2sp^3\right)$ ,  $E_{Coulomb}\left(C_{acetylene}, 2sp^3\right)$ , and  $E_{Coulomb}\left(C_{alkane}, 2sp^3\right)$ ;

$$E_{Coulomb}(atom, msp^3)$$
 is one of  $E_{Coulomb}(C, 2sp^3)$  and  $E_{Coulomb}(Cl, 3sp^3)$ ;

$$E(mol.atom, msp^3) is one of E(C_{ethylene}, 2sp^3), E(C_{ethane}, 2sp^3),$$

$$E(C_{acctylene}, 2sp^3)E(C_{alkane}, 2sp^3);$$

$$E(atom, msp^3)$$
 is one of and  $E(C, 2sp^3)$  and  $E(Cl, 3sp^3)$ ;

$$E_T$$
 (atom – atom,  $msp^3$ ) is one of  $E(C-C,2sp^3)$ ,  $E(C=C,2sp^3)$ , and  $E(C\equiv C,2sp^3)$ ;

5  $atom msp^3$  is one of  $C2sp^3$ ,  $Cl3sp^3$ 

$$E_T$$
  $\left(atom-atom(s_1), msp^3\right)$  is  $E_T$   $\left(C-C, 2sp^3\right)$  and  $E_T$   $\left(atom-atom(s_2), msp^3\right)$  is  $E_T$   $\left(C=C, 2sp^3\right)$ , and

$$r_{msp}$$
 is one of  $r_{C2sp^3}$ ,  $r_{elhane2sp^3}$ ,  $r_{elhylene2sp^3}$ ,  $r_{acetylene2sp^3}$ ,  $r_{alkane2sp^3}$ , and  $r_{Cl3sp^3}$ .

In the case of the  $C2sp^3$  HO, the initial parameters (Eqs. (14.142-14.146)) are

$$r_{2.p^{3}} = \sum_{n=2}^{5} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0} \left(e148.25751 \ eV\right)} = \frac{10e^{2}}{8\pi\varepsilon_{0} \left(e148.25751 \ eV\right)} = 0.91771a_{0}$$
 (15.22)

$$E_{Coulomb}\left(C, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.91771a_{0}} = -14.82575 \,eV \tag{15.23}$$

$$E(magnetic) = \frac{2\pi\mu_0 e^2 h^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.84317a_0)^3} = 0.19086 \ eV$$
 (15.24)

$$E(C,2sp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} + \frac{2\pi\mu_{0}e^{2}h^{2}}{m_{e}^{2}(r_{3})^{3}}$$

$$= -14.82575 \ eV + 0.19086 \ eV$$

$$= -14.63489 \ eV$$
(15.25)

In Eq. (15.18),

15 
$$\sum_{q=Z-n}^{Z-1} (Z-q) = 10$$
 (15.26)

Eqs. (14.147) and (15.17) give

$$E_T$$
 (mol.atom, msp<sup>3</sup>) =  $E_T$  ( $C_{ethane}$ , 2sp<sup>3</sup>) = -151.61569 eV (15.27)

Using Eqs. (15.18-15.28), the final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$ , and the resulting  $E_r(C^{BO}_{-C},C2sp^3)$  of the MO due to charge donation from the HO to the MO where

C-C refers to the bond order of the carbon-carbon bond for different values of the parameter s are given in Table 15.1.

Table 15.1. The final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$  and the resulting 5  $E_r \left( C - C, C2sp^3 \right)$  of the MO due to charge donation from the HO to the MO where C - Crefers to the bond order of the carbon-carbon bond.

MO Bond Order (BO)	s i	s 2	$r_{C2sp^3}(a_0)$ Final	$E_{Coulomb}\left(C2sp^{3}\right)$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	$E_T \left( C - C, C2sp^3 \right)$ (eV)
I	1	0	0.87495	-15.55033	-15.35946	-0.72457
II	2	0	0.85252	-15.95955	-15.76868	-1.13379
Ш	3	0	0.83008	-16.39089	-16.20002	-1.56513
IV	4	0	0.80765	-16.84619	-16.65532	-2.02043

In another generalized case of the basis of forming a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the 10 energy  $E(mol.atom, msp^3)$  of the outer electron of the atom  $msp^3$  shell of each bonding atom must be the average of  $E(mol.atom, msp^3)$  for two different values of s:

$$E(mol.atom, msp^3) = \frac{E(mol.atom(s_1), msp^3) + E(mol.atom(s_2), msp^3)}{2}$$
(15.28)

In this case,  $E_T$  (atom - atom, msp<sup>3</sup>), the energy change of each atom msp<sup>3</sup> shell with the formation of each atom-atom-bond MO, is average for two different values of s:

15 
$$E_T \left( atom - atom, msp^3 \right) = \frac{E_T \left( atom - atom(s_1), msp^3 \right) + E_T \left( atom - atom(s_2), msp^3 \right)}{2}$$
 (15.29)

Consider an aromatic molecule such as benzene given in the Benzene Molecule section. Each C = C double bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon atoms. Each C-H bond of CH having two spin-paired electrons, one from an initially 20 unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO as given by Eq. (13.439). However,  $E_T(atom-atom,msp^3)$  of the C-H-bond MO is given by  $0.5E_T(C=C,2sp^3)$  (Eq. (14.247)) corresponding to one half of a double bond that matches the condition for a single-bond order for C-H that is lowered in energy due to the aromatic 5 character of the bond.

A further general possibility is that a minimum-energy bond is achieved with satisfaction of the potential, kinetic, and orbital energy relationships by the formation of an MO comprising an allowed multiple of a linear combination of  $H_2$ -type ellipsoidal MOs and corresponding HOs or AOs that contribute a corresponding allowed multiple (e.g. 0.5, 0.75, 10 1) of the bond order given in Table 15.1. For example, the alkane MO given in the Continuous-Chain Alkanes section comprises a linear combination of factors of 0.5 of a single bond and 0.5 of a double bond.

Consider a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO comprises another AO or HO having a single bond order or a mixed bond order. Then, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO. Then, in general,  $E_T$  (atom – atom,  $msp^3$ ), the energy change of each atom  $msp^3$  shell with the formation of each atom-atom-bond MO, is a weighted linear sum for different values of s that matches the energy of the bonded MOs, HOs, and AOs:

$$E_{T}\left(atom - atom, msp^{3}\right) = \sum_{n=1}^{N} c_{s_{n}} E_{T}\left(atom - atom\left(s_{n}\right), msp^{3}\right)$$
 (15.30)

where  $c_{s_n}$  is the multiple of the BO of  $s_n$ . The radius  $r_{msp^3}$  of the atom  $msp^3$  shell of each bonding atom is given by the Coulombic energy using the initial energy  $E_{Coulomb}$  (atom,  $msp^3$ ) and  $E_T$  (atom – atom,  $msp^3$ ), the energy change of each atom  $msp^3$  shell with the formation of each atom-atom-bond MO:

$$r_{msp^3} = \frac{-e^2}{8\pi\varepsilon_0 a_0 \left(E_{Coulonb}\left(atom, msp^3\right) + E_T\left(atom - atom, msp^3\right)\right)}$$
(15.31)

where  $E_{Coulomb}(C2sp^3) = -14.825751 \, eV$ . The Coulombic energy  $E_{Coulomb}(mol.atom, msp^3)$  of the outer electron of the  $atom \, msp^3$  shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy  $E(mol.atom, msp^3)$  of the outer electron of the  $atom \, msp^3$  shell is given by the sum of  $E_{Coulomb}(mol.atom, msp^3)$  and E(magnetic) (Eq. (15.20)).  $E_T(atom-atom, msp^3)$ , the energy change of each  $atom \, msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(mol.atom, msp^3)$  and  $E(atom, msp^3)$  given by Eq. (15.21). Using Eq. (15.23) for  $E_{Coulomb}(C, 2sp^3)$  in Eq. (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2.

Table 15.2. The final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$  and the resulting  $E_T\left(C^{BO}_-C,C2sp^3\right)$  of the MO comprising a linear combination of  $H_2$ -type ellipsoidal MOs and corresponding HOs of single or mixed bond order where  $c_{s_n}$  is the multiple of the bond order parameter  $E_T\left(atom-atom(s_n),msp^3\right)$  given in Table 15.1.

Table	15.	1					433			
MO Bond	s 1	<i>C</i> <sub><i>s</i><sub>1</sub></sub>	<i>s</i> 2	$C_{s_2}$	<i>s</i> 3	$c_{s_3}$	$r_{C2sp^3}\left(a_0\right)$	$E_{Coulomb}$ (C2sp <sup>3</sup> ) (eV)	$E\left(C2sp^3\right)$	
Order (BO)							Final	Final	Final	(eV)
1/2I	1	0.5	0	0	0	0	0.89582	-15.18804	-14.99717	-0.36228
1/211	2	0.5	0	0	0	0	0.88392	-15.39265	-15.20178	-0.56689
I + 1/2II	1	0.5	2	0.2 5	0	0	0.87941	-15.47149	-15.28062	-0.64573
1/2II	2	0.2	1	0.2	2	0.2	0.87363	-15.57379	-15.38293	-0.74804
+ (I + II)		5		5		5				
3/4II	2	0.7 5	0	0	0	0	0.86793	-15.67610	-15.48523	-0.85034
I + II	1	0.5	2	0.5	0	0	0.86359	-15.75493	-15.56407	-0.92918
III I +	, 1	0.5	3	0.5	0	0	0.85193	-15.97060	-15.77974	-1.14485
I+ IV	1	0.5	4	0.5	0	0	0.83995	-16.19826	-16.00739	-1.37250
III 111 +	2	0.5	3	0.5	0	0	0.84115	-16.17521	-15.98435	-1.34946
II + IV	2	0.5	4	0.5	0	0	0.82948	-16.40286	-16.21200	-1.57711
IA .	3	0.5	4	0.5	0	0	0.81871	-16.61853	-16.42767	-1.79278
IV +	4	0.5	4	0.5	0	0	0.80765	-16.84619	-16.65532	-2.02043

Consider next the radius of the AO or HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each atom such as 5 carbon superimposes linearly. In general, the radius  $r_{mol2sp^3}$  of the  $C2sp^3$  HO of a carbon atom of a given molecule is calculated using Eq. (14.514) by considering  $\sum E_{T_{mol}} \left(MO, 2sp^3\right)$ , the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by

$$r_{mol 2sp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(E_{Coulomb}\left(C, 2sp^{3}\right) + \sum E_{T_{nol}}\left(MO, 2sp^{3}\right)\right)}$$

$$= \frac{e^{2}}{8\pi\varepsilon_{0} \left(e14.825751 \ eV + \sum \left|E_{T_{nol}}\left(MO, 2sp^{3}\right)\right|\right)}$$
(15.32)

The Coulombic energy  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy  $E(mol.atom, msp^3)$  of the outer electron of the atom  $msp^3$  shell is given by the sum of  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) and E(magnetic) (Eq. (15.20)).

For example, the  $C2sp^3$  HO of each methyl group of an alkane contributes  $10 -0.92918 \, eV$  (Eq. (14.513)) to the corresponding single C-C bond; thus, the corresponding  $C2sp^3$  HO radius is given by Eq. (14.514). The  $C2sp^3$  HO of each methylene group of  $C_nH_{2n+2}$  contributes  $-0.92918 \, eV$  to each of the two corresponding C-C bond MOs. Thus, the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are

$$r_{alkaneC_{onethylone} 2sp^3} = \frac{-e^2}{8\pi\varepsilon_0 \left( E_{Coulomb} \left( C, 2sp^3 \right) + \sum_{C_{T_{alkane}}} \left( methylene \ C - C, 2sp^3 \right) \right)}$$

$$= \frac{e^2}{8\pi\varepsilon_0 \left( e14.825751 \ eV + e0.92918 \ eV + e0.92918 \ eV \right)}$$

$$= 0.81549a_0$$
(15.33)

$$E_{Coulomb} \left( C_{methylene} 2 s p^3 \right) = \frac{-e^2}{8 \pi \varepsilon_0 \left( 0.81549 a_0 \right)} = -16.68412 \ eV \tag{15.34}$$

$$E\left(C_{\text{methylene}} 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}\left(0.81549a_{0}\right)} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}\left(0.84317a_{0}\right)^{3}} = -16.49325 \text{ eV}$$
 (15.35)

In the determination of the parameters of functional groups, heteroatoms bonding to  $C2sp^3$  HOs to form MOs are energy matched to the  $C2sp^3$  HOs. Thus, the radius and the 20 energy parameters of a bonding heteroatom are given by the same equations as those for

 $C2sp^3$  HOs. Using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO,  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>), and  $E\left(C_{mol}2sp^3\right)$  are calculated using  $\sum E_{T_{group}}\left(MO,2sp^3\right)$ , the total energy donation to each bond with which an atom participates in bonding corresponding to the values of  $E_T\left(C^{BO}-C,C2sp^3\right)$  of the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2.

Table 15.3.A. The final values of  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>), and  $E(C_{mol}2sp^3)$  calculated using the values of  $E_T(C_{-C,C2sp^3})$  given in Tables 15.1 and 15.2.

					_	_		_					45	8															
26	25	24	23	22	21	20	19	18	17	16	15	14	13	21	=	10	9	00	7	6	5	4	3	2	1	ion	Designat	ation	Atom Hybridiz
-2.02043	-0.92918	-1.13379	-1.79278	-0.85035	-0.72457	-1.57711	-0.64574	-1.56513	-0.82688	-0.5669	-0.72457	-0.46459	-1.3725	-1.34946	-0.46459	-1.14485	-1.13379	-0.54343	-0.92918	-0.85034	-0.72457	-0.56689	-0.46459	-0.36229	0				$= E_T \left( C - C, C2sp^3 \right)$
0	-0.92918	-0.72457	0	-0.85035	-0.92918	. 0	-0.92918	0	-0.72457	-0.92918	-0.72457	-0.92918	0	0	-0.82688	0	0	-0.54343	0	0	0	0	0	0	0				$E_T\left(C-C,C2sp^3\right)$ $E_T\left(C-C,C2sp^3\right)$
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0				$E_T\left(C-C,C2sp^3\right)$
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0				$E_T\bigg(C-C,C2sp^3\bigg)$
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	. 0	0	0	0				$E_r\left(C-C,C2sp^3\right) \mid E_r\left(C-C,C2sp^3\right)$
0.80765	0.81549	0.81549	0.81871	0.82327	0.82562	0.82948	0.82959	0.83008	0.83078	0.8336	0.836	0.83885	0.83995	0.84115	0.84418	0.85193	0.85252	0.85503	0.86359	0.86793	0.87495	0.88392	0.88983	0.89582	0.91771			,	Final
-16.84619	-16.68412	-16.68411	-16.61853	-16.52645	-16,47951	-16.40286	-16.40067	-16.39089	-16.37721	-16.32183	-16.2749	-16.21952	-16.19826	-16.17521	-16.11722	-15.9706	-15.95955	-15.91261	-15.75493	-15.6761	-15.55033	-15.39265	-15.29034	-15.18804	-14.82575		Final	(eV)	Ecoulomb (mol.atom, msp
-16.65532	-16.49325	-16.49325	-16.42/6/	-16.33339	-10.28803	-10.212	19607'01	-16.2002	-16.18634	-16.13097	-16.08404	-16.02866	-16.00/39	-15.98435	-15.92636	-15.77974	-15.76868	-15.72175	-15.56407	-15.48523	-15.35946	-15.20178	-15.09948	-14.99717	-14.63489			Final	(eV)

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50	49	48	47	46	45	#	43	42	41	40	39	38	37	36	35	34	33	32	31	30	29	28	27
-1.79278	-1.13379	-0.82688	-0.46459	-1.1338	-0.85034	-1.34946	-0.85035	-0.92918	-0.82688	-0.92918	-0.54343	-0.92918	-0.72457	-0.82688	-0.72457	-0.85035	-0.64574	-0.46459	-1.34946	-1.13379	-0.5669	-0.85035	-1.13379
-0.92918	-1.13379	-1.34946	-0.85035	-0.92918	-0.54343	-0.64574	-0.54343	-0.92918	-0.92918	-0.85034	-0.54343	-0.72457	-0.92918	-0.72457	-0.72457	-0.5669	-0.85034	-0.92918	-0.92918	-1.13379	-0.72457	-0.85035	-0.92918
-0.92918	-1.13379	-0.92918	-0.85035	-0.92918	-0.60631	-0.92918	-0.5669	-0.92918	-0.92918	-0.85034	-0.5669	-0.92918	-0.92918	-0.92918	-0.92918	-0.92918	-0.85034	-0.92918	0	0	-0.92918	-0.46459	0
0	0	0	-0.92918	0	-0.92918	0	-0.92918	0	0	0	-0.92918	0	0	0 .	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0		. 0	0	0	0	0	0	0	0	0	0	0	0	0
0.73637	0.74646	0.75877	0.75924	0.7636	0.76631	0.76652	0.76801	0.77247	0.77699	0.77945	0.78155	0.78155	0.78155	0.78617	0.79085	0.79232	0.79232	0.79340	0.79546	0.79597	0.78916	0.80076	0.80561
-18.47690	-18.22712	-17.93128	-17.92022	-17.81791	-17.75502	-17.75013	-17.71561	-17.6133	-17.51099	-17.45561	-17.40869	-17.40869	-17.40868	-17.30638	-17.20408	-17.17218	-17.17217	-17.14871	-17.1044	-17.09334	-17.04641	-16.99104	-16.88872
-18.28604	-18.03626	-17.74041	-17.72936	-17.62705	-17.56415	-17.55927	-17.52475	-17.42244	-17.32013	-17.26475	-17.21783	-17.21783	-17.21782	-17.11552	-17.01322	-16.98132	-16.98131	-16.95784	-16.91353	-16.90248	-16.85554	-16.80018	-16.69786

Table 15.3.B. The final values of  $r_{Atom,HO,AO}$ ,  $E_{Coulomb}$  (mol.atom,msp<sup>3</sup>), and  $E(C_{mol}2sp^3)$  calculated for heterocyclic groups using the values of  $E_T(C^{BO}_T-C,C2sp^3)$  given in Tables 15.1 and 15.2.

												ÐΙ														<u> </u>
25	24	23	22	21	20	19	18	17	16	15	14	13	น	11	10	9	8	7	6	5	4	3	2	1	Designation	Atom Hybridization
-0.85034	-0.85034	-0.92918	-0.85034	-0.54343	-0.85035	-0.85035	-1.13379	-0.85034	-0.85035	-1.13379	-1.13379	-0.92918	-0.85035	-0.92918	-0.92918	-0.72457	-0.46459	-0.60631	-1.13379	-0.54343	-0.92918	-0.72457	-0.56690	0		$E_{r}\left(C-C,C2sp^{3}\right)$
-0.54343	-0.54343	-0.92918	-0.28345	-0.54343	-0.56690	-0.54343	-1.13380	-0.85034	-0.85035	-0.92918	-0.724S7	-0.92918	-0.85035	-0.72457	-0.60631	-0.72457	-0.92918	-0.60631	0	-0.54343	0	0	0	0		$E_r\bigg(C-C,C2sp^3\bigg)$
-0.60631	-0.56690	-0.92918	-0.54343	-0.56690	-0.92918	0.00000	0	-0.56690	-0.46459	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$E_T \left( C - C, C2sp \right)$
-0.92918	-0.92918	0	-0.92918	-0.92918	0	-0.92918	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$E_T\bigg(C-C,C2sp^3\bigg)$
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$ E_r \left( C - C, C2sp^3 \right) $
0.76631	0.76801	0.77247	0.78050	0.78155	0.79232	0.79340	0.79597	0.79597	0.80076	0.80561	0.81549	0.81549	0.82327	0.82562	0.83159	0.83600	0.83885	0.84833	0.85252	0.85503	0.86359	0.87495	0.88392	0.91771	Final	Y Atom. HO. AO
-17.75502	-17.71560	-17.61330	-17.43216	-17.40869	-17.17218	-17.14871	-17.09334	-17.09334	-16.99103	-16.88873	-16.68412	-16.68411	-16.52644	-16,47951	-16.36125	-16.27490	-16.21953	-16.03838	-15.95954	-15.91261	-15.75493	-15.55033	-15.39265	-14.82575	(eV) Final	Ecoulosob (mol atom, msp³)
-17.56416	-17.52474	-17.42243	-17.24130	-17.21783	-16.98132	-16.95785	-16.90248	-16.90247	-16.80017	-16.69786	-16,49325	-16.49325	-16.33558	-16.28864	-16.17038	-16.08404	-16.02866	-15.84752	-15.76868	-15.72175	-15.56407	-15,35946	-15,20178	-14.63489	(eV) Final	$E\left(C_{mol}2sp^3\right)$
	<b>-0.85034 -0.54343 -0.60631 -0.92918</b> 0 0.76631 <b>-17.75502</b>	-0.85034         -0.54343         -0.56690         -0.92918         0         0.76801         -17.71560           -0.85034         -0.54343         -0.60631         -0.92918         0         0.76631         -17.75502	-0.92918         -0.92918         -0.92918         0         0         0.77247         -17.61330           -0.85034         -0.54343         -0.56690         -0.92918         0         0.76801         -17.75502           -0.85034         -0.54343         -0.60631         -0.92918         0         0.76631         -17.75502	-0.85034         -0.28345         -0.54343         -0.92918         0         0.78050         -17.43216           -0.92918         -0.92918         0         0         0.77247         -17.61330           -0.85034         -0.54343         -0.56690         -0.92918         0         0.76801         -17.71560           -0.85034         -0.54343         -0.60631         -0.92918         0         0.76631         -17.75502	-0.54343       -0.54343       -0.56690       -0.92918       0       0.78155       -17.40869         -0.85034       -0.28345       -0.54343       -0.92918       0       0.78050       -17.43216         -0.92918       -0.92918       0       0       0.77247       -17.61330         -0.85034       -0.54343       -0.56690       -0.92918       0       0.76801       -17.75502	-0.85035         -0.56690         -0.92918         0         0         0.79232         -17.17218           -0.54343         -0.54343         -0.56690         -0.92918         0         0.78155         -17.40869           -0.85034         -0.28345         -0.54343         -0.92918         0         0.78050         -17.43216           -0.85034         -0.54343         -0.92918         0         0         0.77247         -17.61330           -0.85034         -0.54343         -0.56690         -0.92918         0         0.76801         -17.75502	-0.85035         -0.54343         0.00000         -0.92918         0         0.79340         -17.14871           -0.85035         -0.56690         -0.92918         0         0         0.79232         -17.17218           -0.54343         -0.54343         -0.56690         -0.92918         0         0.78155         -17.40869           -0.85034         -0.28345         -0.54343         -0.92918         0         0.78050         -17.43216           -0.85034         -0.54343         -0.92918         0         0         0.77247         -17.61330           -0.85034         -0.54343         -0.56690         -0.92918         0         0.76801         -17.71560           -0.85034         -0.54343         -0.56690         -0.92918         0         0.76801         -17.71560	-1.13379         -1.13380         0         0         0         0.79597         -17.09334           -0.85035         -0.54343         0.00000         -0.92918         0         0.79340         -17.14871           -0.85035         -0.56690         -0.92918         0         0         0.79232         -17.17218           -0.54343         -0.54343         -0.56690         -0.92918         0         0.78155         -17.40869           -0.85034         -0.28345         -0.54343         -0.92918         0         0.78050         -17.43216           -0.85034         -0.54343         -0.56690         -0.92918         0         0.77247         -17.61330           -0.85034         -0.54343         -0.56690         -0.92918         0         0.76801         -17.71560           -0.85034         -0.54343         -0.56690         -0.92918         0         0.76801         -17.71560	-0.85034         -0.85034         -0.56690         0         0         0.79597         -17.09334           -1.13379         -1.13380         0         0         0         0         0.79597         -17.09334           -0.85035         -0.54343         0.00000         -0.92918         0         0.799340         -17.14871         -17.17218           -0.85035         -0.56690         -0.92918         0         0         0.79232         -17.17218         -17.40869           -0.85034         -0.54343         -0.56690         -0.92918         0         0.78050         -17.43216         -17.43216           -0.85034         -0.92918         0         0         0.77247         -17.61330         -17.71560           -0.85034         -0.54343         -0.56690         -0.92918         0         0         0.77247         -17.61330           -0.85034         -0.54343         -0.56690         -0.92918         0         0         0.776801         -17.71560           -0.85034         -0.54343         -0.56690         -0.92918         0         0         0.776801         -17.71560	-0.85035         -0.85035         -0.46459         0         0         0.80076         -16.99103           -0.85034         -0.85034         -0.56690         0         0         0.79597         -17.09334           -1.13379         -1.13380         0         0         0         0         0.79597         -17.09334           -0.85035         -0.54343         0.00000         -0.92918         0         0.799340         -17.14871           -0.85035         -0.54343         -0.92918         0         0         0.79932         -17.17218           -0.85034         -0.54343         -0.56690         -0.92918         0         0.78050         -17.40869           -0.85034         -0.28345         -0.54343         -0.92918         0         0.78050         -17.43216           -0.85034         -0.54343         -0.92918         0         0         0.77247         -17.61330           -0.85034         -0.54343         -0.56690         -0.92918         0         0.76801         -17.71560           -0.85034         -0.54343         -0.56690         -0.92918         0         0         0.77247         -17.61330           -0.85034         -0.54343         -0.56690         -0.92918<	-1.13379         -0.92918         0         0         0         0.80561         -16.8873           -0.85035         -0.85035         -0.46459         0         0         0.80076         -16.99103           -0.85034         -0.85034         -0.56690         0         0         0.79597         -17.09334           -0.85035         -0.54343         0.00000         0         0         0.79597         -17.09334           -0.85035         -0.54343         0.00000         -0.92918         0         0.79934         -17.14871           -0.85034         -0.56690         -0.92918         0         0.79932         -17.17218           -0.85034         -0.54343         -0.56690         -0.92918         0         0.78050         -17.40869           -0.85034         -0.28345         -0.54343         -0.92918         0         0.77247         -17.61330           -0.85034         -0.54343         -0.92918         0         0.77801         -17.71560           -0.85034         -0.54343         -0.56690         -0.92918         0         0.77801         -17.71560           -0.85034         -0.54343         -0.56690         -0.92918         0         0.77801         -17.71560	-1,13379         -0,72457         0         0         0         0,81549         -16,88412           -1,13379         -0,92918         0         0         0         0,80561         -16,88873           -0,85035         -0,85035         -0,85035         -0,46459         0         0         0,80076         -16,99103           -0,85034         -0,85035         -0,85039         0         0         0         0,79597         -17,09334           -0,85035         -0,54343         0,00000         0         0         0,79597         -17,09334           -0,85035         -0,54343         0,00000         -0,92918         0         0         0,79597         -17,19334           -0,85035         -0,54343         -0,00000         -0,92918         0         0,79597         -17,14871           -0,85035         -0,54343         -0,56690         -0,92918         0         0,79532         -17,17218           -0,85034         -0,23345         -0,54343         -0,92918         0         0,78050         -17,49326           -0,85034         -0,54343         -0,92918         0         0,78050         -17,43216         -17,74320           -0,85034         -0,54343         -0,92918	-0.97918         -0.97918         -0.97918         0         0         0.81549         -16.68411           -1.13379         -0.77457         0         0         0         0.81549         -16.68412           -1.13379         -0.92918         0         0         0         0.80561         -16.88873           -0.85035         -0.85035         -0.46459         0         0         0.80076         -16.99103           -0.85034         -0.85034         -0.56690         0         0         0         0.79597         -17.09334           -0.85035         -0.54343         0.00000         -0.92918         0         0         0.79597         -17.09334           -0.85035         -0.54343         0.00000         -0.92918         0         0.79597         -17.19334         -17.17218           -0.85034         -0.56690         -0.92918         0         0.79322         -17.17218         -17.40869           -0.85034         -0.28345         -0.56690         -0.92918         0         0.78050         -17.43216           -0.85034         -0.54343         -0.92918         0         0.77801         -17.1330           -0.85034         -0.54343         -0.92918         0 <t< td=""><td>-0.85035         -0.85035         -0.85035         0         0         0         0.82327         -16.52644           -0.92918         -0.92918         0         0         0         0.81549         -16.68411         -16.68411           -1.13379         -0.92918         0         0         0         0.81549         -16.68412         -16.68412           -1.13379         -0.92918         0         0         0         0.80561         -16.88873         -16.99103           -0.85034         -0.85034         -0.56690         0         0         0.80076         -16.99103         -17.09334           -0.85035         -0.54343         0.00000         -0.92918         0         0         0.79597         -17.09334         -17.14871         -17.17218           -0.85035         -0.54343         -0.00000         -0.92918         0         0         0.79340         -17.14871         -17.17218           -0.85034         -0.54343         -0.56690         -0.92918         0         0.78050         -17.40869         -17.40869         -17.40869         -17.40869         -17.40869         -17.40869         -17.61330         -17.61330         -17.61330         -17.761330         -17.761330         -17.75502         -1</td><td>-0.92918         -0.72457         0         0         0         082562         -16.47951           -0.85035         -0.85035         0         0         0         0         0.82327         -16.52644           -0.92918         -0.92918         0         0         0         0         0.82327         -16.52644           -0.92918         -0.92918         0         0         0         0         0.81549         -16.68411           -1.13379         -0.72457         0         0         0         0         0.81549         -16.68412           -0.85035         -0.85035         -0.46459         0         0         0         0.80076         -16.99103           -0.85034         -0.85034         -0.56690         0         0         0         0.99597         -17.09334           -0.85035         -0.54343         0.00000         -0.92918         0         0         0.79597         -17.09334           -0.85034         -0.54343         -0.56690         -0.92918         0         0.79930         -17.14871         -17.14871           -0.92918         -0.92918         0         0         0.78050         -17.40869         -17.40869           -0.85034</td><td>-0.92918         -0.60631         0         0         0         083159         -1636125           -0.92918         -0.72457         0         0         0         0         082562         -16.47951           -0.92918         -0.92918         0         0         0         0         0.82327         -16.52644           -0.92918         -0.92918         0         0         0         0         0.82327         -16.52644           -0.92918         -0.92918         0         0         0         0         0.82327         -16.68411           -1.13379         -0.92918         0         0         0         0.81549         -16.68412           -1.13379         -0.85034         -0.85034         -0.56690         0         0         0.80076         -16.88873           -0.85034         -0.85034         -0.56690         0         0         0         0.79997         -17.09334           -0.85035         -0.56390         -0.92918         0         0         0         0.79997         -17.09334           -0.85034         -0.54343         -0.56690         -0.92918         0         0         0.79932         -17.17816           -0.85034         -0.543</td><td>-0.72457         -0.72457         -0.72457         0         0         0.83600         -16.27490           -0.92918         -0.60631         0         0         0         0         0.83159         -16.36125           -0.92918         -0.72457         0         0         0         0         0.83159         -16.36125           -0.92918         -0.72457         0         0         0         0         0.82562         -16.47951           -0.92918         -0.92918         0         0         0         0         0.82327         -16.58411           -0.92918         -0.92918         0         0         0         0         0.81549         -16.68411           -1.13379         -0.72918         0         0         0         0         0.81549         -16.68412           -1.13379         -0.85034         -0.85034         -0.56690         0         0         0         0.8076         -16.99103           -0.85034         -0.56390         0         0         0         0.79597         -17.09334         -17.14871         -17.109334           -0.85034         -0.56390         -0.92918         0         0         0.79332         -17.14969</td><td>-0.46459         -0.92918         0         0         0.83885         -16.21953           -0.772457         -0.72457         0         0         0         0.83800         -16.27490           -0.92918         -0.60631         0         0         0         0.83159         -16.36125           -0.92918         -0.72457         0         0         0         0.83159         -16.36125           -0.92918         -0.85035         0         0         0         0         0.82562         -16.47951           -0.92918         -0.92918         0         0         0         0         0.82327         -16.58441           -0.92918         -0.92918         0         0         0         0         0.81549         -16.58411           -1.13379         -0.92918         0         0         0         0         0.81549         -16.58412           -1.13379         -0.85034         -0.85035         -0.46459         0         0         0         0.80076         -16.99103           -0.88034         -0.85034         -0.56690         0         0         0         0.79997         -17.09344           -0.88034         -0.54343         -0.56690         -0.92918&lt;</td><td>-0.60631         -0.60631         0         0         0         0.84833         -16.03838           -0.46459         -0.292918         0         0         0         0         0.83885         -16.21953           -0.772457         -0.72457         0         0         0         0         0.83885         -16.21953           -0.92918         -0.60631         0         0         0         0         0.83159         -16.27490           -0.92918         -0.76457         0         0         0         0         0.82562         -16.47951           -0.92918         -0.72457         0         0         0         0         0.82562         -16.68411           -0.92918         -0.72918         0         0         0         0         0.82562         -16.68412           -1.13379         -0.72918         0         0         0         0         0.82564         -16.68412           -1.13379         -0.72918         0         0         0         0         0.8076         -16.99103           -0.85034         -0.85035         -0.85034         -0.56690         0         0         0         0.79937         -17.09334           -0.85034</td><td>-1,13379         0         0         0         0         0         085222         -15.9594           -0,00631         -0,00631         -0,00631         0         0         0         0,04833         -16.03838           -0,46459         -0,92918         0         0         0         0,04833         -16.21953           -0,72457         -0,72457         0         0         0         0,83805         -16.27490           -0,92918         -0,50931         0         0         0         0,83805         -16.27490           -0,92918         -0,50931         0         0         0         0,83509         -16.56123           -0,52918         -0,72457         0         0         0         0,82562         -16.47951           -0,52918         -0,72918         0         0         0         0,82562         -16.68411           -1,13379         -0,72918         0         0         0         0,81549         -16.68412           -0,85034         -0,86903         -0,46459         0         0         0,80561         -16.88873           -1,13379         -1,13380         0         0         0         0,79597         -17.09344</td><td>-0.54343         -0.54343         -0.54343         0.         0         0.85503         -15.91261           -1.13379         0         0         0         0         0.82522         -15.95944           -0,60631         -0         0         0         0.82522         -15.95944           -0,76437         -0,60631         0         0         0         0.82522         -15.95944           -0,77447         -0,72457         0         0         0         0.83885         -16.21953           -0,92918         -0,72457         0         0         0         0.83805         -16.21953           -0,92918         -0,72457         0         0         0         0.83502         -16.26125           -0,92918         -0,92918         0         0         0         0.83502         -16.26412           -0,92918         -0,92918         0         0         0         0.81549         -16.26412           -1,13379         -0,72457         0         0         0         0.80561         -16.88873           -1,13379         -0,82035         -0,46459         0         0         0.80561         -16.88873           -0,86035         -0,54343         -0,06690</td><td>-0.92918         0         0         0         0         0         0         0.8839         -157.5493           -0.54343         -0.54343         0         0         0         0         0.88503         -1591261           -0.56313         -0.54343         0         0         0         0.88503         -1591261           -0.66313         -0.66311         0         0         0         0.88232         -16.21953           -0.76457         -0.92918         0         0         0         0         0.88885         -16.21953           -0.92918         -0.72457         0         0         0         0         0.83159         -16.36125           -0.92918         -0.72457         0         0         0         0         0.83252         -16.56125           -0.92918         -0.72457         0         0         0         0         0.83252         -16.56125           -0.92918         -0.92918         0         0         0         0         0.83252         -16.56412           -1.13379         -0.72918         0         0         0         0.81549         -16.68412         -16.68412           -0.85034         -0.86093         -0</td><td>-0.72457         0         0         0         0         0.8795         -15.5503           -0.52918         0         0         0         0         0         0.8795         -15.75493           -0.54343         -0.54343         0         0         0         0.82503         -15.91261           -0.54343         -0.54343         0         0         0         0         0.82503         -15.91261           -1.13379         -0.60631         0         0         0         0         0.82522         -15.9954           -0.72437         -0.72457         0         0         0         0         0.83885         -16.21953           -0.72437         -0.72457         0         0         0         0         0.83885         -16.21953           -0.72437         -0.72457         0         0         0         0         0.83885         -16.21953           -0.72437         -0.72457         0         0         0         0         0.82527         -16.2644           -0.72918         0         0         0         0         0.82227         -16.68411         -16.68411           -1.13379         -0.726918         0         0         <t< td=""><td>  -0.56690   0   0   0   0   0   0   0   0   0  </td><td>  1.00</td><td>  Pinal   (e'y)</td></t<></td></t<>	-0.85035         -0.85035         -0.85035         0         0         0         0.82327         -16.52644           -0.92918         -0.92918         0         0         0         0.81549         -16.68411         -16.68411           -1.13379         -0.92918         0         0         0         0.81549         -16.68412         -16.68412           -1.13379         -0.92918         0         0         0         0.80561         -16.88873         -16.99103           -0.85034         -0.85034         -0.56690         0         0         0.80076         -16.99103         -17.09334           -0.85035         -0.54343         0.00000         -0.92918         0         0         0.79597         -17.09334         -17.14871         -17.17218           -0.85035         -0.54343         -0.00000         -0.92918         0         0         0.79340         -17.14871         -17.17218           -0.85034         -0.54343         -0.56690         -0.92918         0         0.78050         -17.40869         -17.40869         -17.40869         -17.40869         -17.40869         -17.40869         -17.61330         -17.61330         -17.61330         -17.761330         -17.761330         -17.75502         -1	-0.92918         -0.72457         0         0         0         082562         -16.47951           -0.85035         -0.85035         0         0         0         0         0.82327         -16.52644           -0.92918         -0.92918         0         0         0         0         0.82327         -16.52644           -0.92918         -0.92918         0         0         0         0         0.81549         -16.68411           -1.13379         -0.72457         0         0         0         0         0.81549         -16.68412           -0.85035         -0.85035         -0.46459         0         0         0         0.80076         -16.99103           -0.85034         -0.85034         -0.56690         0         0         0         0.99597         -17.09334           -0.85035         -0.54343         0.00000         -0.92918         0         0         0.79597         -17.09334           -0.85034         -0.54343         -0.56690         -0.92918         0         0.79930         -17.14871         -17.14871           -0.92918         -0.92918         0         0         0.78050         -17.40869         -17.40869           -0.85034	-0.92918         -0.60631         0         0         0         083159         -1636125           -0.92918         -0.72457         0         0         0         0         082562         -16.47951           -0.92918         -0.92918         0         0         0         0         0.82327         -16.52644           -0.92918         -0.92918         0         0         0         0         0.82327         -16.52644           -0.92918         -0.92918         0         0         0         0         0.82327         -16.68411           -1.13379         -0.92918         0         0         0         0.81549         -16.68412           -1.13379         -0.85034         -0.85034         -0.56690         0         0         0.80076         -16.88873           -0.85034         -0.85034         -0.56690         0         0         0         0.79997         -17.09334           -0.85035         -0.56390         -0.92918         0         0         0         0.79997         -17.09334           -0.85034         -0.54343         -0.56690         -0.92918         0         0         0.79932         -17.17816           -0.85034         -0.543	-0.72457         -0.72457         -0.72457         0         0         0.83600         -16.27490           -0.92918         -0.60631         0         0         0         0         0.83159         -16.36125           -0.92918         -0.72457         0         0         0         0         0.83159         -16.36125           -0.92918         -0.72457         0         0         0         0         0.82562         -16.47951           -0.92918         -0.92918         0         0         0         0         0.82327         -16.58411           -0.92918         -0.92918         0         0         0         0         0.81549         -16.68411           -1.13379         -0.72918         0         0         0         0         0.81549         -16.68412           -1.13379         -0.85034         -0.85034         -0.56690         0         0         0         0.8076         -16.99103           -0.85034         -0.56390         0         0         0         0.79597         -17.09334         -17.14871         -17.109334           -0.85034         -0.56390         -0.92918         0         0         0.79332         -17.14969	-0.46459         -0.92918         0         0         0.83885         -16.21953           -0.772457         -0.72457         0         0         0         0.83800         -16.27490           -0.92918         -0.60631         0         0         0         0.83159         -16.36125           -0.92918         -0.72457         0         0         0         0.83159         -16.36125           -0.92918         -0.85035         0         0         0         0         0.82562         -16.47951           -0.92918         -0.92918         0         0         0         0         0.82327         -16.58441           -0.92918         -0.92918         0         0         0         0         0.81549         -16.58411           -1.13379         -0.92918         0         0         0         0         0.81549         -16.58412           -1.13379         -0.85034         -0.85035         -0.46459         0         0         0         0.80076         -16.99103           -0.88034         -0.85034         -0.56690         0         0         0         0.79997         -17.09344           -0.88034         -0.54343         -0.56690         -0.92918<	-0.60631         -0.60631         0         0         0         0.84833         -16.03838           -0.46459         -0.292918         0         0         0         0         0.83885         -16.21953           -0.772457         -0.72457         0         0         0         0         0.83885         -16.21953           -0.92918         -0.60631         0         0         0         0         0.83159         -16.27490           -0.92918         -0.76457         0         0         0         0         0.82562         -16.47951           -0.92918         -0.72457         0         0         0         0         0.82562         -16.68411           -0.92918         -0.72918         0         0         0         0         0.82562         -16.68412           -1.13379         -0.72918         0         0         0         0         0.82564         -16.68412           -1.13379         -0.72918         0         0         0         0         0.8076         -16.99103           -0.85034         -0.85035         -0.85034         -0.56690         0         0         0         0.79937         -17.09334           -0.85034	-1,13379         0         0         0         0         0         085222         -15.9594           -0,00631         -0,00631         -0,00631         0         0         0         0,04833         -16.03838           -0,46459         -0,92918         0         0         0         0,04833         -16.21953           -0,72457         -0,72457         0         0         0         0,83805         -16.27490           -0,92918         -0,50931         0         0         0         0,83805         -16.27490           -0,92918         -0,50931         0         0         0         0,83509         -16.56123           -0,52918         -0,72457         0         0         0         0,82562         -16.47951           -0,52918         -0,72918         0         0         0         0,82562         -16.68411           -1,13379         -0,72918         0         0         0         0,81549         -16.68412           -0,85034         -0,86903         -0,46459         0         0         0,80561         -16.88873           -1,13379         -1,13380         0         0         0         0,79597         -17.09344	-0.54343         -0.54343         -0.54343         0.         0         0.85503         -15.91261           -1.13379         0         0         0         0         0.82522         -15.95944           -0,60631         -0         0         0         0.82522         -15.95944           -0,76437         -0,60631         0         0         0         0.82522         -15.95944           -0,77447         -0,72457         0         0         0         0.83885         -16.21953           -0,92918         -0,72457         0         0         0         0.83805         -16.21953           -0,92918         -0,72457         0         0         0         0.83502         -16.26125           -0,92918         -0,92918         0         0         0         0.83502         -16.26412           -0,92918         -0,92918         0         0         0         0.81549         -16.26412           -1,13379         -0,72457         0         0         0         0.80561         -16.88873           -1,13379         -0,82035         -0,46459         0         0         0.80561         -16.88873           -0,86035         -0,54343         -0,06690	-0.92918         0         0         0         0         0         0         0.8839         -157.5493           -0.54343         -0.54343         0         0         0         0         0.88503         -1591261           -0.56313         -0.54343         0         0         0         0.88503         -1591261           -0.66313         -0.66311         0         0         0         0.88232         -16.21953           -0.76457         -0.92918         0         0         0         0         0.88885         -16.21953           -0.92918         -0.72457         0         0         0         0         0.83159         -16.36125           -0.92918         -0.72457         0         0         0         0         0.83252         -16.56125           -0.92918         -0.72457         0         0         0         0         0.83252         -16.56125           -0.92918         -0.92918         0         0         0         0         0.83252         -16.56412           -1.13379         -0.72918         0         0         0         0.81549         -16.68412         -16.68412           -0.85034         -0.86093         -0	-0.72457         0         0         0         0         0.8795         -15.5503           -0.52918         0         0         0         0         0         0.8795         -15.75493           -0.54343         -0.54343         0         0         0         0.82503         -15.91261           -0.54343         -0.54343         0         0         0         0         0.82503         -15.91261           -1.13379         -0.60631         0         0         0         0         0.82522         -15.9954           -0.72437         -0.72457         0         0         0         0         0.83885         -16.21953           -0.72437         -0.72457         0         0         0         0         0.83885         -16.21953           -0.72437         -0.72457         0         0         0         0         0.83885         -16.21953           -0.72437         -0.72457         0         0         0         0         0.82527         -16.2644           -0.72918         0         0         0         0         0.82227         -16.68411         -16.68411           -1.13379         -0.726918         0         0 <t< td=""><td>  -0.56690   0   0   0   0   0   0   0   0   0  </td><td>  1.00</td><td>  Pinal   (e'y)</td></t<>	-0.56690   0   0   0   0   0   0   0   0   0	1.00	Pinal   (e'y)

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-1.133/9	11777	-1 12270	-0.0000	35030 0	1.13360	1 13390
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0	0	Ž	-0.92918		0	
0	0		0		0	
0.74646	0.75493		0.75924		0.76360	
-18.22713	-18.02252		-17.92022		-17.81791	
-18.03627	-17.83166		-17.72935		-17.62705	

The energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO. The force constant k' 5 (Eq. (15.1)) is used to determine the ellipsoidal parameter c' (Eq. (15.2)) of the each  $H_2$ -type-ellipsoidal-MO in terms of the central force of the foci. Then, c' is substituted into the energy equation (from Eq. (15.11))) which is set equal to  $n_1$  times the total energy of  $H_2$  where  $n_1$  is the number of equivalent bonds of the MO and the energy of  $H_2$ ,  $-31.63536831 \, eV$ , Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO. From the energy equation and the relationship between the axes, the dimensions of the MO are solved. The energy equation has the semimajor axis a as it only parameter. The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)). The parameter solutions then allow for the component and total energies of the MO to be determined.

The total energy,  $E_T(H_1MO)$ , is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus  $E_T(AO/HO)$ :

$$E_T(H_2MO) = V_e + T + V_m + V_p + E_T(AO/HO)$$
 (15.36)

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_{T}(AO/HO)$$
(15.37)

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the group,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and  $E_T(AO/HO)$  is the total energy comprising the difference of the energy E(AO/HO) of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component  $\Delta E_{H_2MO}(AO/HO)$  due to the AO or HO's charge donation to the MO.

$$E_{T}(AO/HO) = E(AO/HO) - \Delta E_{H_{2}MO}(AO/HO)$$
 (15.38)

As specific examples given in previous sections,  $E_T(AO/HO)$  is one from the group of

$$\begin{split} E_{T} \big( AO \, / \, HO \big) &= E \big( O2p \ shell \big) = -E (ionization; \ O) = -13.6181 \ eV \ ; \\ E_{T} \big( AO \, / \, HO \big) &= E \big( N2p \ shell \big) = -E (ionization; \ N) = -14.53414 \ eV \ ; \\ E_{T} \big( AO \, / \, HO \big) &= E \big( C, 2sp^{3} \big) = -14.63489 \ eV \ ; \\ E_{T} \big( AO \, / \, HO \big) &= E_{Coulomb} \big( Cl, 3sp^{3} \big) = -14.60295 \ eV \ ; \\ E_{T} \big( AO \, / \, HO \big) &= E (ionization; \ C) + E (ionization; \ C^{+}) \ ; \end{split}$$

$$E_{T}(AO/HO) = E(C_{ethane}, 2sp^{3}) = -15.35946 \ eV;$$

$$E_T(AO/HO) = +E(C_{ethylene}, 2sp^3) - E(C_{ethylene}, 2sp^3)$$

 $E_T(AO/HO) = E(C_{alkang}, 2sp^3) = -15.56407 eV$ .

$$E_T(AO/HO) = E(C,2sp^3) - 2E_T(C=C,2sp^3) = -14.63489 \ eV - (-2.26758 \ eV);$$

10 
$$E_T(AO/HO) = E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) = 16.20002 \ eV;$$
 $E_T(AO/HO) = E(C, 2sp^3) - 2E_T(C = C, 2sp^3) = -14.63489 \ eV - (-3.13026 \ eV);$ 
 $E_T(AO/HO) = E(C_{benzene}, 2sp^3) - E(C_{benzene}, 2sp^3);$ 
 $E_T(AO/HO) = E(C, 2sp^3) - E_T(C = C, 2sp^3) = -14.63489 \ eV - (-1.13379 \ eV),$  and

To solve the bond parameters and energies, 
$$c' = a \sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (Eq.

(15.2)) is substituted into  $E_T(\mu_1 MO)$  to give

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}(AO/HO)$$

The total energy is set equal to  $E(basis\ energies)$  which in the most general case is given by

465 the sum of a first integer  $n_1$  times the total energy of  $H_2$  minus a second integer  $n_2$  times the total energy of H, minus a third integer  $n_3$  times the valence energy of E(AO) (e.g.  $E(N) = -14.53414 \, eV$ ) where the first integer can be 1,2,3..., and each of the second and third integers can be 0,1,2,3....

 $E(basis\ energies) = n_1(-31.63536831\ eV) - n_2(-13.605804\ eV) - n_3E(AO)$  (15.40) 5 In the case that the MO bonds two atoms other than hydrogen,  $E(basis\ energies)$  is  $n_1$  times the total energy of  $H_2$  where  $n_1$  is the number of equivalent bonds of the MO and the energy of  $H_2$ ,  $-31.63536831 \, eV$ , Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

10 
$$E(basis\ energies) = n_1(-31.63536831\ eV)$$
 (15.41)

 $E_{\tau}(\mu_{1}M0)$ , is set equal to  $E(basis\ energies)$ , and the semimajor axis a is solved. Thus, the semimajor axis a is solved from the equation of the form:

$$-\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}\left[c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right)\ln\frac{a+\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a-\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}-1\right]+E_{T}\left(AO/HO\right)=E(basis\ energies)\ (15.42)$$

The distance from the origin of the  $H_2$ -type-ellipsoidal-MO to each focus c', the internuclear 15 distance 2c', and the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO b=c are solved from the semimajor axis a using Eqs. (15.2-15.4). Then, the component energies are given by Eqs. (15.6-15.9) and (15.39).

The total energy of the MO of the functional group,  $E_T$  (40), is the sum of the total energy of the components comprising the energy contribution of the MO formed between the 20 participating atoms and  $E_r$  (atom-atom, msp<sup>3</sup>.AO), the change in the energy of the AOs or HOs upon forming the bond. From Eqs. (15.39-15.40),  $E_T$  (MO) is

$$E_{T}(MO) = E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO)$$
 (15.43)

During bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the sum of the Doppler,  $\overline{E}_{D}$ , and 25 average vibrational kinetic energies,  $\bar{E}_{Kvib}$ :

$$\overline{E}_{osc} = n_{\rm l} \left( \overline{E}_D + \overline{E}_{Kvib} \right) = n_{\rm l} \left( E_{hv} \sqrt{\frac{2\overline{E}_K}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
(15.44)

where  $n_1$  is the number of equivalent bonds of the MO, k is the spring constant of the equivalent harmonic oscillator, and  $\mu$  is the reduced mass. The angular frequency of the reentrant oscillation in the transition state corresponding to  $\overline{E}_D$  is determined by the force 5 between the central field and the electrons in the transition state. The force and its derivative are given by

$$f(R) = -c_{BO} \frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}$$
 (15.45)

and

$$f'(a) = 2c_{BO} \frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}$$
 (15.46)

10 such that the angular frequency of the oscillation in the transition state is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{1o}C_{2o}e^2}{4\pi\epsilon_0 R^3}}{m_e}}$$
(15.47)

where R is the semimajor axis a or the semiminor axis b depending on the eccentricity of the bond that is most representative of the oscillation in the transition state,  $c_{BO}$  is the bond-order factor which is 1 for a single bond and when the MO comprises  $n_1$  equivalent single bonds as in the case of functional groups.  $c_{BO}$  is 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules and 9 for an independent triplet bond.  $C_{1o}$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and  $C_{2o}$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond. Typically,  $C_{1o} = C_1$  and  $C_{2o} = C_2$ . The kinetic energy,  $E_K$ , corresponding to  $\overline{E}_D$  is given by Planck's equation for functional groups:

$$\overline{E}_{\kappa} = \hbar \omega = \hbar \sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{\frac{m_e}{m_e}}$$
(15.48)

The Doppler energy of the electrons of the reentrant orbit is

$$\overline{E}_{D} \cong E_{hv} \sqrt{\frac{2\overline{E}_{K}}{m_{e}c^{2}}} = E_{hv} \sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{0}R^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}$$

$$(15.49)$$

 $\overline{E}_{asc}$  given by the sum of  $\overline{E}_{D}$  and  $\overline{E}_{Kvib}$  is

$$\overline{E}_{osc}(group) = n_1 \left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1 \left(E_{hv} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}}{m_e} + E_{vib}}\right) \tag{15.50}$$

 $E_{hv}$  of a group having  $n_1$  bonds is given by  $E_T$  (MO)/  $n_1$  such that

$$\overline{E}_{osc} = n_1 \left( \overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left( E_T \left( \omega_0 \right) / n_1 \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.51)

 $E_{T+asc}$  (Group) is given by the sum of  $E_{T}$  (MO) (Eq. (15.42)) and  $\bar{E}_{asc}$  (Eq. (15.51)):

$$E_{T+asc}$$
 (Group)=  $E_{T}$  (MO)+  $\overline{E}_{asc}$ 

$$= \left( \left( -\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[ c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] \right)$$

$$= \left( \left( -\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[ c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] \right)$$

$$= \left( \left( -\frac{aa_{0}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \right) + E_{T}\left(atom - atom, msp^{3}.AO\right) \right)$$

$$= \left( \left( -\frac{aa_{0}}{2C_{1}C_{2}} \right) + \left( -\frac{aa_{0}}{a} \right) + \left( -\frac{aa_{0}}{2C_{1}C_{2}} \right) + \left( -\frac{aa_{0}}{2C_$$

$$= \left(E(basis\ energies) + E_T\left(atom-atom, msp^3.AO\right)\right) \left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{\frac{m_e}{m_ec^2}}}\right] + n_1 \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

The total energy of the functional group  $E_T(group)$  is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms,  $E(basis\ energies)$ , the change in the energy of the AOs or HOs upon forming the bond  $(E_T(atom-atom,msp^3.AO))$ , the energy of oscillation in the transition state, and the change in magnetic energy with bond formation,  $E_{mag}$ . From Eq. (15.52), the total energy of the group  $E_T(group)$  is

$$E_{T}(Group) = \left(E(basis\ energies) + E_{T}(atom-atom, msp^{3}.AO) \left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right]\right) (15.53)$$

$$+ n_{1}\bar{E}_{Kvib} + E_{mag}$$

The change in magnetic energy  $E_{mag}$  which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by

10 
$$E_{mag} = c_3 \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} = c_3 \frac{8\pi\mu_0 \mu_B^2}{r^3}$$
 (15.54)

where  $r^3$  is the radius of the atom that reacts to form the bond and  $c_3$  is the number of electron pairs.

$$E_{T} (Group) = \left(E(basis\ energies) + E_{T} \left(atom - atom, msp^{3}.AO\right)\right) \left[1 + \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}} \frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}}{m_{e}}}\right] + n_{1}\overline{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}}\right) (15.55)$$

The total bond energy of the group  $E_D$  ( $c_{roup}$ ) is the negative difference of the total energy of the group (Eq. (15.55)) and the total energy of the starting species given by the sum of  $c_4 E_{initial}$  ( $c_4 AO / HO$ ) and  $c_5 E_{initial}$  ( $c_5 AO / HO$ ):

$$E_{D} (Group) = -\left(E(basis\ energies) + E_{T} \left(atom - atom, msp^{3}.AO\right)\right)\left[1 + \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}} - \left(c_{4}E_{lmilal}\left(AO/HO\right) + c_{5}E_{lmilal}\left(c_{5}AO/HO\right)\right)\right]$$

$$(15.56)$$

In the case of organic molecules, the atoms of the functional groups are energy matched to the  $C2sp^3$  HO such that

$$E(AO/HO) = -14.63489 eV$$
 (15.57)

5 For examples of  $E_{mag}$  from previous sections:

$$E_{mog}\left(C2sp^{3}\right) = c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} = c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{\left(0.91771a_{o}\right)^{3}} = c_{3}0.14803 \ eV$$
 (15.58)

$$E_{mag}(O2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{a_0^3} = c_3 0.11441 \ eV$$
 (15.59)

$$E_{mag}(N2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{\left(0.93084a_0\right)^3} = c_3 0.14185 \ eV$$
 (15.60)

In the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.42) to arrive at a. Then, the remaining parameters are determined using Eqs. (15.1-15.5). Next, the energies are given by Eqs. (15.52-15.59). To meet the equipotential condition for the union of the  $H_2$ -type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO in principal Eqs. 15 (15.42) and (15.52) may given by

(i) one: 
$$c_2 = 1$$
 (15.61)

20 (ii) the ratio that is less than one of  $13.605804 \, eV$ , the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the

Coulombic energy of the participating AO or HO of the atom,  $E_{Coulomb}$  (MO.atom, msp<sup>3</sup>) given by Eqs. (15.19) and (15.31-15.32). For  $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right>$ 13.605804 eV:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}} = \frac{13.605804\ eV}{\left|E_{Coulomb}\left(MO.atom, msp^{3}\right)\right|}$$
(15.62)

For  $\left| E_{Coulomb} \left( MO.atom, msp^3 \right) \right| < 13.605804 eV$ :

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\,AorBsp^{3}}}}{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}} = \frac{\left|E_{Coulomb}\left(MO.atom, msp^{3}\right)\right|}{13.605804 \, eV}$$
(15.63)

(iii) the ratio that is less than one of 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the valence energy, E(valence), of the participating AO or HO of the atom where E(valence) is 10 the ionization energy or  $E(MO.atom, msp^3)$  given by Eqs. (15.20) and (15.31-15.32). For  $|E(valence)| > 13.605804 \ eV$ :

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}} = \frac{13.605804\ eV}{|E(valence)|}$$
(15.64)

For |E(valence)| < 13.605804 eV:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}}{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}} = \frac{|E(valence)|}{13.605804\ eV}$$
(15.65)

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5

(iv) the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom,  $E_{Coulomb} \left(MO.atom, msp^3\right)$  given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy, E(valence), of the participating AO or HO of a second atom to which the first is energy matched where E(valence) is the

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ionization energy or  $E(MO.atom, msp^3)$  given by Eqs. (15.20) and (15.31-15.32). For  $|E_{Conlomb}(MO.atom, msp^3)| > E(valence)$ :

$$c_2 = \frac{|E(valence)|}{|E_{Caulomb}(MO.atom, msp^3)|}$$
(15.66)

For  $|E_{Coulomb}(MO.atom, msp^3)| < E(valence)$ :

 $c_2 = \frac{\left| E_{Coulomb} \left( MO.atom, msp^3 \right) \right|}{\left| E(valence) \right|}$  (15.67)

(v) the ratio that is less than one of the magnitude of the valence-level energies,  $E_n(valence)$ , of the AO or HO of the nth participating atom of two that are energy matched where E(valence) is the ionization energy or  $E(MO.atom, msp^3)$  given by Eqs. (15.20) and 10 (15.31-15.32):

$$c_2 = \frac{E_1(valence)}{E_2(valence)} \tag{15.68}$$

(vi) the factor that is the ratio of the hybridization factor  $c_2(1)$  of the valence AO or HO of a first atom and the hybridization factor  $c_2(2)$  of the valence AO or HO of a second atom to which the first is energy matched where  $c_2(n)$  is given by Eqs. (15.62-15.68); alternatively  $c_2$  is the hybridization factor  $c_2(1)$  of the valence AOs or HOs a first pair of atoms and the hybridization factor  $c_2(2)$  of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = \frac{c_2(1)}{c_2(2)} \tag{15.69}$$

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(vii) the factor that is the product of the hybridization factor  $c_2(1)$  of the valence AO or HO of a first atom and the hybridization factor  $c_2(2)$  of the valence AO or HO of a second atom to which the first is energy matched where  $c_2(n)$  is given by Eqs. (15.62-15.69);

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alternatively  $c_2$  is the hybridization factor  $c_2(1)$  of the valence AOs or HOs a first pair of atoms and the hybridization factor  $c_2(2)$  of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2) (15.70)$$

5 The hybridization factor  $c_2$  corresponds to the force constant k (Eqs. (11.65) and (13.58)). In the case that the valence or Coulombic energy of the AO or HO is less than 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), then  $C_2$  corresponding to k' (Eq. (15.1)) is given by Eqs. (15.62-15.70).

Specific examples of the factors  $c_2$  and  $C_2$  of a  $H_2$ -type ellipsoidal MO of Eq. 10 (15.51) given in following sections are

$$c_{2}(C2sp^{3}HO \text{ to } F) = \frac{E(C,2sp^{3})}{E(F)}c_{2}(C2sp^{3}HO) = \frac{-14.63489 \text{ eV}}{-17.42282 \text{ eV}}(0.91771) = 0.77087;$$

$$C_{2}(C2sp^{3}HO \text{ to } CI) = \frac{E(CI)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-12.96764 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.81317;$$

$$C_{2}(C2sp^{3}HO \text{ to } Br) = \frac{E(Br)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-11.81381 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.74081;$$

$$C_{2}(C2sp^{3}HO \text{ to } I) = \frac{E(I)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-10.45126 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.65537;$$

$$15 \quad c_{2}(C2sp^{3}HO \text{ to } O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.85395;$$

$$c_{2}(H \text{ to } 1^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})} = \frac{-14.53414 \text{ eV}}{-15.35946 \text{ eV}} = 0.94627;$$

$$c_{2}(C2sp^{3}HO \text{ to } N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.91140;$$

$$c_{2}(H \text{ to } 2^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})} = \frac{-14.53414 \text{ eV}}{-15.56407 \text{ eV}} = 0.93383;$$

$$C_{2}(S3p \text{ to } H) = \frac{E(S,3p)}{E(H)} = \frac{-10.36001 \text{ eV}}{-13.60580 \text{ eV}} = 0.76144;$$

$$20 \quad C_{2}(C2sp^{3}HO \text{ to } S) = \frac{E(S)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.64965;$$

$$c_{2}(O \text{ to } S3sp^{3} \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(S)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771);$$

$$= 1.20632$$

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \ eV}{-13.60580 \ eV} = 0.85045;$$

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}\left(0.85045\right) = 0.66951;$$

$$C_{2}(S3sp^{3} \text{ to O to } C2sp^{3}HO) = \frac{E(S,3sp^{3})}{E(O,2p)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}}(0.91771);$$

$$= 0.77641$$

$$c_{2}(O \text{ to } N2p \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(N)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}}(0.91771);$$

$$= 0.85987$$

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727;$$

$$C_2$$
 (benzeneC2sp<sup>3</sup>HO)= $c_2$  (benzeneC2sp<sup>3</sup>HO)= $\frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252$ ;

$$c_{2}(arylC2sp^{3}HO \text{ to } O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}}(0.85252)$$

$$c_2(H \text{ to anline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171;$$

$$c_{2}(arylC2sp^{3}HO \text{ to } N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.85252) ,$$

and

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$$C_2 \left( S3p \text{ to aryl-type } C2sp^3 HO \right) = \frac{E(S,3p)}{E(C,2sp^3)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700.$$

### MO INTERCEPT ANGLES AND DISTANCES

Consider the general case of Eqs. (13.84-13.95) wherein the nucleus of a B atom and the 5 nucleus of a A atom comprise the foci of each  $H_2$ -type ellipsoidal MO of an A-B bond. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the A-atom AO are determined from the polar equation of the ellipse:

$$r = r_0 \frac{1+e}{1+e\cos\theta'} \tag{15.71}$$

The radius of the A shell is  $r_A$ , and the polar radial coordinate of the ellipse and the radius of 10 the A shell are equal at the point of intersection such that

$$r_{A} = \left(a - c'\right) \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a}\cos\theta'}$$
 (15.72)

The polar angle  $\theta'$  at the intersection point is given by

$$\theta' = \cos^{-1} \left( \frac{a}{c'} \left( (a - c') \frac{1 + \frac{c'}{a}}{a_0} - 1 \right) \right)$$
 (15.73)

Then, the angle  $\theta_{AAO}$  the radial vector of the A AO makes with the internuclear axis is

$$\theta_{AAO} = 180^{\circ} - \theta' \tag{15.74}$$

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals such that the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the A radial vector obeys the following relationship:

$$r_A \sin \theta_{AAO} = b \sin \theta_{H,MO} \tag{15.75}$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{r_a \sin \theta_{AAO}}{h} \tag{15.76}$$

The distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H,MO} = a\cos\theta_{H,MO} \tag{15.77}$$

The distance  $d_{AAO}$  along the internuclear axis from the origin of the A atom to the point of 5 intersection of the orbitals is given by

$$d_{AAO} = c' - d_{H,MO} (15.78)$$

### **BOND ANGLES**

Further consider an ACB MO comprising a linear combination of C-A-bond and C-B10 bond MOs where C is the general central atom. A bond is also possible between the A and B atoms of the C-A and C-B bonds. Such A-B bonding would decrease the C-A and C-B bond strengths since electron density would be shifted from the latter bonds to the former bond. Thus, the  $\angle ACB$  bond angle is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal A and B atoms is zero. The 15 force constant k' of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_o} \tag{15.79}$$

where  $C_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the molecule which is 0.75 (Eq. (13.59)) for a terminal A - H (A is H or other atom) and 1 20 otherwise and  $C_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.42) and (15.52). The distance from the origin of the MO to each focus c' of the A - B ellipsoidal MO is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (15.80)

25 The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.81}$$

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The length of the semiminor axis of the prolate spheroidal A - B MO b = c is given by Eq. (15.4).

The component energies and the total energy,  $E_T(n,mo)$ , of the A-B bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of  $H_2$  except 5 that the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor which is 1 for a single bond and when the MO comprises  $n_1$  equivalent single bonds as in the case of functional groups.  $c_{BO}$  is 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules. The kinetic energy term is multiplied by  $c'_{BO}$  which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. The electron energy terms are multiplied by  $c_1$ , 10 the fraction of the  $H_2$ -type ellipsoidal MO basis function of a terminal chemical bond which is 0.75 (Eq. (13.233)) for a terminal A-H (A is H or other atom) and 1 otherwise. The electron energy terms are further multiplied by  $c'_2$ , the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond. Furthermore, when A-B comprises atoms other than H, 15  $E_T$  (atom – atom, msp<sup>3</sup>.AO), the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give  $E_T$  (n, mo):

$$E_{T}(\mu_{2}MO) = \frac{-e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c_{2}' \left( 2c_{BO} - c'_{BO} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + E_{T} \left( atom - atom, msp^{3}.AO \right)$$

$$(15.82)$$

The radiation reaction force in the case of the vibration of A-B in the transition state 20 corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy that includes the radiation reaction of the A-B MO is given by the sum of  $E_T(\mu_2MO)$  (Eq. (15.82)) and  $\overline{E}_{osc}$  given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy  $E_T(A-B)$  of the A-B MO including the Doppler term is

$$E_{T}(A-B) = \begin{bmatrix} \left(\frac{-e^{2}}{8\pi\varepsilon_{0}c'}\left[c_{1}c_{2}'\left(2c_{BO}-c'_{BO}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] + E_{T}\left(atom-atom,msp^{3}.AO\right) \right] \\ \left[ \left(\frac{2\hbar\sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}\right] + \frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_{1}c_{2}'e^{2}}{8\pi\varepsilon_{o}a^{3}} - \frac{c_{BO}e^{2}}{8\pi\varepsilon_{o}(a+c')^{3}}}{\mu} \right] \\ (15.83) \end{bmatrix}$$

where  $C_{1o}$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of the oscillatory transition state of the A-B bond which is 0.75 (Eq. (13.233)) in the case of H bonding to a central atom and 1 otherwise,  $C_{2o}$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond, and  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  is the reduced mass of the nuclei given by Eq. (11.154). To match the boundary condition that the total energy of the A-B ellipsoidal MO is zero,  $E_T(A-B)$  given by Eq. (15.83) is set equal to zero. Substitution of Eq. (15.81) into Eq. (15.83) gives

$$10 \quad 0 = \begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} c_{1}c_{2}'\left(2c_{BO} - c'_{BO}\frac{a_{0}}{a}\right) \ln\frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1\right) + E_{T}\left(atom - atom, msp^{3}.AO\right) \\ \left[ \frac{2\hbar\sqrt{\frac{c_{1}C_{2}e^{2}}{4\pi\varepsilon_{0}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}} \right] + \frac{1}{2}\hbar\sqrt{\frac{c_{1}c_{2}'e^{2}}{8\pi\varepsilon_{0}a^{3}} - \frac{c_{BO}e^{2}}{8\pi\varepsilon_{0}\left(a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}\right)}}{\mu}}$$

$$(15.84)$$

The vibrational energy-term of Eq. (15.84) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)). The electron-central-field force and its derivative are given by

$$f(a) = -c_{BO} \frac{c_1 c_2' e^2}{4\pi\varepsilon_0 a^3}$$
 (15.85)

and

$$f'(a) = 2c_{BO} \frac{c_1 c_2' e^2}{4\pi\varepsilon_0 a^3}$$
 (15.86)

The nuclear repulsion force and its derivative are given by

$$f\left(a+c'\right) = \frac{e^2}{8\pi\varepsilon_o\left(a+c'\right)^2} \tag{15.87}$$

and

5 
$$f'(a+c') = -\frac{e^2}{4\pi\varepsilon_o(a+c')^3}$$
 (15.88)

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_1c_2'e^2}{4\pi\varepsilon_0a^3} - \frac{e^2}{8\pi\varepsilon_0(a+c')^2}}$$
(15.89)

Since both terms of  $\overline{E}_{ox} = \overline{E}_D + \overline{E}_{Kvib}$  are small due to the large values of a and c', to very good approximation, a convenient form of Eq. (15.84) which is evaluated to determine the bond angles of functional groups is given by

$$0 = \begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} & c_{1}c_{2}'\left(2 - \frac{a_{0}}{a}\right) \ln\frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \\ -\frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} & \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \end{bmatrix} + E_{T}\left(atom - atom, msp^{3}.AO\right) \\ -\frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} & \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - \frac{e^{2}}{8\pi\varepsilon_{0}a^{3}} - \frac{e^{2}}{8\pi\varepsilon_{0}\left(a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}\right)} \\ -\frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - \frac{1}{2\hbar\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}$$

From the energy relationship given by Eq. (15.90) and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the A-B MO can be solved. The most convenient way to solve Eq. (15.90) is by the reiterative technique using a computer.

A factor  $c_2$  of a given atom in the determination of  $c_2'$  for calculating the zero of the total A-B bond energy is typically given by Eqs. (15.62-15.65). In the case of a H-H terminal bond of an alkyl or alkenyl group,  $c_2'$  is typically the ratio of  $c_2$  of Eq. (15.62) for the H-H bond which is one and  $c_2$  of the carbon of the corresponding C-H bond:

$$c_2' = \frac{1}{c_2(C2sp^3)} = \frac{13.605804 \, eV}{E_{Coulomb} \left(C - H \, C2sp^3\right)}$$
(15.91)

In the case of the determination of the bond angle of the ACH MO comprising a linear combination of C-A-bond and C-H-bond MOs where A and C are general, C is the central atom, and  $c_2$  for an atom is given by Eqs. (15.62-15.70),  $c_2'$  of the A-H terminal bond is typically the ratio of  $c_2$  of the A atom for the A-H terminal bond and  $c_2$  of the C atom of the corresponding C-H bond:

$$c_2' = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)(msp^3)}$$
(15.92)

In the case of the determination of the bond angle of the COH MO of an alcohol comprising a linear combination of C-O-bond and O-H-bond MOs where C, O, and H are carbon, 10 oxygen, and hydrogen, respectively,  $c'_2$  of the C-H terminal bond is typically 0.91771 since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively) that is energy matched to the  $C2sp^3$  HO.

In the determination of the hybridization factor  $c_2'$  of Eq. (15.90) from Eqs. (15.62-15.70), the Coulombic energy,  $E_{Coulomb} \left( MO.atom, msp^3 \right)$ , or the energy,  $E \left( MO.atom, msp^3 \right)$ , the radius  $r_{A-B.AorB.\phi^3}$  of the A or B AO or HO of the heteroatom of the A-B terminal bond MO such as the  $C2sp^3$  HO of a terminal C-C bond is calculated using Eq. (15.32) by considering  $\sum E_{T_{mol}} \left( MO.2sp^3 \right)$ , the total energy donation to each bond with which it participates in bonding as it forms the terminal bond. The Coulombic energy  $E_{Coulomb} \left( MO.atom, msp^3 \right)$  of the outer electron of the atom  $msp^3$  shell is given by Eq. (15.19).

- 20 In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy  $E(MO.atom, msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by the sum of  $E_{Coulomb}(MO.atom, msp^3)$  and E(magnetic) (Eq. (15.20)).
- In the specific case of the terminal bonding of two carbon atoms, the  $c_2$  factor of each carbon given by Eq. (15.62) is determined using the Coulombic energy  $E_{Coulomb} \left(C C \ C2sp^3\right)$  of the outer electron of the  $C2sp^3$  shell given by Eq. (15.19) with the

radius  $r_{C-C\ C2sp^3}$  of each  $C2sp^3$  HO of the terminal C-C bond calculated using Eq. (15.32) by considering  $\sum E_{T_{mol}}\left(MO,2sp^3\right)$ , the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy, 0.92918 eV (Eq. (14.513)), corresponding to the terminal C-C bond. 5 The corresponding  $E_T\left(atom-atom,msp^3.AO\right)$  in Eq. (15.90) is  $E_T\left(C-C\ C2sp^3\right)=-1.85836\ eV$ .

In the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus,  $c'_2$  is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

10 
$$c_2' = \frac{1}{2} \left( c_2' \left( atom \ 1 \right) + c_2' \left( atom \ 2 \right) \right)$$
 (15.93)

In the exemplary cases of C-C, O-O, and N-N where C is carbon:

$$c_{2}' = \frac{1}{2} \left( \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-A_{1}AO/HO}}} + \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-A_{1}AO/HO}}} \right)$$

$$= \frac{1}{2} \left( \frac{13.605804 \ eV}{E_{Coulomb} \left( A - A.A_{1}AO/HO \right)} + \frac{13.605804 \ eV}{E_{Coulomb} \left( A - A.A_{2}AO/HO \right)} \right)$$
(15.94)

In the exemplary cases of C-N, C-O, and C-S,

$$c_2' = \frac{1}{2} \left( \frac{13.605804 \ eV}{E_{Coulomb} \left( C - B \ C2sp^3 \right)} + c_2 \left( C \ to \ B \right) \right)$$
 (15.95)

where C is carbon and  $c_2(C \text{ to } B)$  is the hybridization factor of Eqs. (15.52) and (15.84) that matches the energy of the atom B to that of the atom C in the group. For these cases, the corresponding  $E_T(atom-atom,msp^3.AO)$  term in Eq. (15.90) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.56)) are

20 
$$E_T(C - O C2sp^3.O2p) = -1.44915 eV;$$
  $E_T(C - O C2sp^3.O2p) = -1.65376 eV;$   $E_T(C - N C2sp^3.N2p) = -1.44915 eV;$   $E_T(C - S C2sp^3.S2p) = -0.72457 eV;$   $E_T(O - O O2p.O2p) = -1.44915 eV;$   $E_T(O - O O2p.O2p) = -1.65376 eV;$ 

$$E_{T}(N-N N2p.N2p) = -1.44915 \ eV; \qquad E_{T}(N-O N2p.O2p) = -1.44915 \ eV;$$

$$E_{T}(F-F F2p.F2p) = -1.44915 \ eV; \qquad E_{T}(Cl-Cl \ Cl3p.Cl3p) = -0.92918 \ eV;$$

$$E_{T}(Br-Br \ Br4p.Br4p) = -0.92918 \ eV; \qquad E_{T}(I-I \ I5p.I5p) = -0.36229 \ eV;$$

$$E_{T}(C-F \ C2sp^{3}.F2p) = -1.85836 \ eV; \qquad E_{T}(C-Cl \ C2sp^{3}.Cl3p) = -0.92918 \ eV;$$

$$E_{T}(C-Br \ C2sp^{3}.Br4p) = -0.72457 \ eV; \qquad E_{T}(C-I \ C2sp^{3}.I5p) = -0.36228 \ eV, \quad \text{and}$$

$$E_{T}(O-Cl \ O2p.Cl3p) = -0.92918 \ eV.$$

In the case that the terminal bond is X-X where X is a halogen atom,  $c_1$  is one, and  $c_2'$  is the average (Eq. (15.93)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.62-15.63) where  $E_{Coulomb}\left(MO.atom, msp^3\right)$  is determined using Eq. 10 (15.32) and  $E_{Coulomb}\left(MO.atom, msp^3\right)=13.605804\ eV$  for X=I. The factor  $C_1$  of Eq. (15.90) is one for all halogen atoms. The factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I,  $C_2$  is the hybridization factor of Eq. (15.52) given by 15 Eq. (15.70) with  $c_2\left(1\right)$  being that of the halogen given by Eq. (15.68) that matches the valence energy of X ( $E_1\left(valence\right)$ ) to that of the  $C2sp^3$  HO ( $C_2\left(valence\right)=-14.63489\ eV$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $C_2\left(2\right)=0.91771$ , Eq. (13.430)).  $E_T\left(atom-atom, msp^3.AO\right)$  of Eq. (15.90) is the maximum for the participating atoms which is  $-1.44915\ eV$ ,  $-0.92918\ eV$ ,  $-0.92918\ eV$ , and  $-0.33582\ eV$  for F, Cl, Br, and I, 20 respectively.

Consider the case that the terminal bond is C-X where C is a carbon atom and X is a halogen atom. The factors  $c_1$  and  $c_2$  of Eq. (15.90) are one for all halogen atoms. For X=F,  $c_2'$  is the average (Eq. (15.95)) of the hybridization factors of the participating carbon and F atoms where  $c_2$  for carbon is given by Eq. (15.62) and  $c_2$  for fluorine matched to 25 carbon is given by Eq. (15.70) with  $c_2$  (1) for the fluorine atom given by Eq. (15.68) that matches the valence energy of F ( $E_1(valence) = -17.42282 \ eV$ ) to that of the  $C2sp^3$  HO

 $(E_2(valence) = -14.63489 \, eV$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO  $(c_2(2) = 0.91771, \, \text{Eq. } (13.430))$ . The factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of 5 the other halogens, Cl, Br, and I,  $c_2'$  is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom.  $C_2$  of the terminal-atom bond matches that used to determine the energies of the corresponding C-X-bond MO. Then,  $C_2$  is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with  $c_2(1)$  for the halogen atom given by Eq. (15.68) that matches the valence energy of X ( $E_1(valence)$ ) to 10 that of the  $C2sp^3$  HO ( $C_2(valence) = -14.63489 \, eV$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2(2) = 0.91771$ , Eq. (13.430)).  $E_T(atom-atom, msp^3.AO)$  of Eq. (15.90) is the maximum for the participating atoms which is  $-1.85836 \, eV$ ,  $-0.92918 \, eV$ ,  $-0.72457 \, eV$ , and  $-0.33582 \, eV$  for F, Cl, Br, and I, respectively.

Consider the case that the terminal bond is H-X corresponding to the angle of the atoms HCX where C is a carbon atom and X is a halogen atom. The factors  $c_1$  and  $c_2$  of Eq. (15.90) are 0.75 for all halogen atoms. For X=F,  $c_2'$  is given by Eq. (15.69) with  $c_2$  of the participating carbon and F atoms given by Eq. (15.62) and Eq. (15.65), respectively. The factor  $c_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of E0 given by Eq. (1.243). For each of the other halogens, E1, E2, and E3 is also given by Eq. (15.69) with E3 of the participating carbon given by Eq. (15.62) and E3 of the participating E4 atom given by E5 atom given by E6. In these cases, E6 is given by Eq. (15.65) for the corresponding atom E2 where E3 matches the energy of the atom E3 to that of E4.

Using the distance between the two atoms A and B of the general molecular group ACB when the total energy of the corresponding A-B MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^2 + s_2^2 - 2s_1 s_2 \cos ine \theta = s_3^2$$
 (15.96)

With  $s_1 = 2c'_{C-A}$ , the internuclear distance of the C-A bond,  $s_2 = 2c'_{C-B}$ , the internuclear distance of each C-B bond, and  $s_3=2c_{A-B}^{\dagger}$ , the internuclear distance of the two terminal atoms, the bond angle  $\theta_{\angle ACB}$  between the C-A and C-B bonds is given by

$$(2c'_{C-A})^2 + (2c'_{C-B})^2 - 2(2c'_{C-A})(2c'_{C-B})\cos \theta = (2c'_{A-B})^2$$
(15.97)

5 
$$\theta_{\angle ACB} = \cos^{-1}\left(\frac{\left(2c'_{C-A}\right)^2 + \left(2c'_{C-B}\right)^2 - \left(2c'_{A-B}\right)^2}{2\left(2c'_{C-A}\right)\left(2c'_{C-B}\right)}\right)$$
 (15.98)

Consider the exemplary structure  $C_b C_a (O_a) O_b$  wherein  $C_a$  is bound to  $C_b$ ,  $O_a$ , and  $O_b$ . In the general case that the three bonds are coplanar and two of the angles are known, say  $\theta_1$  and  $\theta_2$ , then the third  $\theta_3$  can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \tag{15.99}$$

10 In the general case that two of the three coplanar bonds are equivalent and one of the angles is known, say  $\theta_1$ , then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{(360 - \theta_1)}{2} \tag{15.100}$$

# ANGLES AND DISTANCES FOR AN MO THAT FORMS AN ISOSCELES

#### 15 TRIANGLE

In the general case where the group comprises three A-B bonds having B as the central atom at the apex of a pyramidal structure formed by the three bonds with the A atoms at the base in the xy-plane. The  $C_{3\nu}$  axis centered on B is defined as the vertical or z-axis, and any two A-B bonds form an isosceles triangle. Then, the angle of the bonds and the distances 20 from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416):

the distance  $d_{origin-B}$  from the origin to the nucleus of a terminal B atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60^{\circ}} \tag{15.101}$$

the height along the z-axis from the origin to the A nucleus  $d_{height}$  is given by

25 
$$d_{height} = \sqrt{(2c'_{A-B})^2 - (d_{origin-B})^2}$$
, and (15.102)

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the angle  $\theta_{\nu}$  of each A-B bond from the z-axis is given by

$$\theta_{v} = \tan^{-1} \left( \frac{d_{\text{origin-}B}}{d_{\text{height}}} \right) \tag{15.103}$$

Consider the case where the central atom B is further bound to a fourth atom C and the B-C bond is along the z-axis. Then, the bond  $\theta_{\angle ABC}$  given by Eq. (14.206) is

$$\theta_{\angle ABC} = 180 - \theta_{\nu} \tag{15.104}$$

## DIHEDRAL ANGLE

Consider the plane defined by a general ACA MO comprising a linear combination of two C-A-bond MOs where C is the central atom. The dihedral angle  $\theta_{\angle BC/ACA}$  between the 10 ACA-plane and a line defined by a third bond with C, specifically that corresponding to a C-B-bond MO, is calculated from the bond angle  $\theta_{\angle ACA}$  and the distances between the A, B, and C atoms. The distance  $d_1$  along the bisector of  $\theta_{\angle ACA}$  from C to the internuclear-distance line between A and A,  $2c'_{A-A}$ , is given by

$$d_1 = 2c'_{C-A}\cos\frac{\theta_{\angle ACA}}{2} \tag{15.105}$$

15 where  $2c'_{C-A}$  is the internuclear distance between A and C. The atoms A, A, and B define the base of a pyramid. Then, the pyramidal angle  $\theta_{\angle ABA}$  can be solved from the internuclear distances between A and A,  $2c'_{A-A}$ , and between A and B,  $2c'_{A-B}$ , using the law of cosines (Eq. (15.98)):

$$\theta_{\angle ABA} = \cos^{-1}\left(\frac{\left(2c'_{A-B}\right)^2 + \left(2c'_{A-B}\right)^2 - \left(2c'_{A-A}\right)^2}{2\left(2c'_{A-B}\right)\left(2c'_{A-B}\right)}\right)$$
(15.106)

20 Then, the distance  $d_2$  along the bisector of  $\theta_{\angle ABA}$  from B to the internuclear-distance line  $2c'_{A-A}$ , is given by

$$d_2 = 2c'_{A-B}\cos\frac{\theta_{\angle ABA}}{2} \tag{15.107}$$

The lengths  $d_1$ ,  $d_2$ , and  $2c'_{C-B}$  define a triangle wherein the angle between  $d_1$  and the internuclear distance between B and C,  $2c'_{C-B}$ , is the dihedral angle  $\theta_{\angle BC/ACA}$  that can be solved using the law of cosines (Eq. (15.98)):

$$\theta_{\angle BC/ACA} = \cos^{-1} \left( \frac{d_1^2 + (2c'_{C-B})^2 - d_2^2}{2d_1(2c'_{B-C})} \right)$$
(15.108)

## SOLUTION OF GEOMETRICAL AND ENERGY PARAMETERS OF MAJOR FUNCTIONAL GROUPS AND CORRESPONDING ORGANIC 5 MOLECULES

The exemplary molecules given in the following sections were solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies where linearly added to achieve the molecular solutions. Each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination. Each functional group element was solved using the atomic orbital and hybrid orbital spherical orbitsphere solutions bridged by molecular orbitals comprised of the  $H_2$ -type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs. The energy  $E_{mog}$  (e.g. given 15 by Eq. (15.58)) for a  $C2sp^3$  HO and Eq.(15.59) for an O2p AO) was subtracted for each set

of unpaired electrons created by bond breakage.

The bond energy is not equal to the component energy of each bond as it exists in the molecule; although, they are close. The total energy of each group is its contribution to the total energy of the molecule as a whole. The determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage. Also, the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group. This will effect the functional-group energy. But, because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they were neglected.

The energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (13.428)). The intercept angles are determined from Eqs.

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(15.71-15.78) using the final radius of the HO of each atom. The final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined. This final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the corresponding final radius. The radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell. The donation of electron density to the AOs and HOs reduces the energy. The donation of the electron density to the MO's at each AO or HO is that which causes the resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.

The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. New stable compositions of matter can be predicted as well as the structures of combinatorial chemistry reactions. Further important pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the molecules to be identified from the common spatial charge-density functions of a series of active molecules. Drugs can be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the 20 drug.

To calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given molecule are used to calculate the fields, and from the fields, the interactions between groups of the same molecule or between groups on different molecules are calculated wherein the interactions are distance and relative orientation dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

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## AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple  $H_2$ -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule  $(C_6H_6)$  section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

 $C_6H_6$  can be considered a linear combination of three ethylene molecules wherein a C-H bond of each  $CH_2$  group of  $H_2C=CH_2$  is replaced by a C=C bond to form a six-10 member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule  $(CH_2CH_2)$  section. The radius  $r_{ethylene2sp}$ ,  $(0.85252a_0)$  of the  $C2sp^3$  shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy  $E_{Coulomb}(C_{elhylone}, 2sp^3)$  (-15.95955 eV) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.245). The energy  $E(C_{ethylene}, 2sp^3)$  (-15.76868 eV) of the outer electron of the  $C2sp^3$  shell 15 is given by Eq. (14.246).  $E_T(C=C,2sp^3)$  (-1.13380 eV) (Eq. (14.247), the energy change of each  $C2sp^3$  shell with the formation of the C=C-bond MO is given by the difference between  $E(C_{ethylene}, 2sp^3)$  and  $E(C, 2sp^3)$ .  $C_6H_6$  can be solved using the same principles as those used to solve ethylene wherein the 2s and 2p shells of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two C2sp3 hybridized orbitals 20 (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each 2sp3 HO of each carbon atom initially has four unpaired electrons. Thus, the 6 H atomic orbitals (AOs) of benzene contribute six electrons and the six  $sp^3$ -hybridized carbon atoms contribute twenty-four electrons to form six C-H bonds and six C = C bonds. Each C - H bond has two paired electrons with one donated from the H AO 25 and the other from the  $C2sp^3$  HO. Each C=C bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two C2sp3 HOs of the participating carbon atoms. Each C-H and each C=C bond comprises a linear combination of one and two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively. 30

Consider the case where three sets of C = C-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution per bond from each  $C2sp^3$  HO to the C=C-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond C=C-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as 5 those used to determine the same parameters of the C=C-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each C = C-bond gives rise to the  $C_{bernene} 2sp^3$  HO-shell Coulombic energy  $E_{Coulomb} \left( C_{bernene}, 2sp^3 \right)$  given by Eq. (14.245). To meet the equipotential condition of the union of the six  $C2sp^3$  HOs,  $c_2$  and  $c_3$  of Eq. (15.42) for the

10 aromatic C=C-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of  $E_{Coulomb}\left(C_{benzene},2sp^3\right)$  (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2$$
 (benzeneC2sp³HO) =  $c_2$  (benzeneC2sp³HO) =  $\frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252$  (15.143)

The energies of each C=C bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the C=C bonding of benzene wherein each of the six C=C bonds of benzene comprises (0.75)(4)=3 electrons according to Eq. (15.142). The total energy of the bonds of the eighteen electrons of the C=C bonds of benzene,  $E_T \left( C_6 H_6, C=C \right)$ , is given by (6)(0.75) times  $E_{T+asc} \left( C=C \right)$  (Eq. (14.492)), the total energy of the C=C-bond MO of benzene including the Doppler term, minus eighteen times  $E\left( C,2sp^3 \right)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each C that forms the C=C bonds of bond order two. Thus, the total energy of the six C=C bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$E_{T}\left(C_{6}H_{6},C=C\right) = (6)(0.75)E_{T+asc}\left(C=C\right) - (6)(3)E\left(C,2sp^{3}\right)$$

$$= (6)(0.75)\left(-66.05796 \ eV\right) - 18\left(-14.63489 \ eV\right)$$

$$= -297.26081 \ eV - \left(-263.42798 \ eV\right)$$

$$= -33.83284 \ eV$$
(15.144)

25 The results of benzene can be generalized to the class of aromatic and heterocyclic compounds.  $E_{hr}$  of an aromatic bond is given by  $E_{\tau}(H_2)$  (Eqs. (11.212) and (14.486)), the maximum total energy of each  $H_2$ -type MO such that

$$\bar{E}_{o\infty} = n_1 \left( \bar{E}_D + \bar{E}_{Kvib} \right) = n_1 \left( -31.63536831 \, eV \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \tag{15.145}$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two 30 given in the Benzene Molecule ( $C_6H_6$ ) section modifies Eqs. (15.52-15.56). Multiplication of

the total energy given by Eq. (15.55) by  $f_1 = 0.75$  with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_{T} (Group) = f_{1} \left( \frac{E(basis\ energies) + E_{T} (atom - atom, msp^{3}.AO)}{2\hbar \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}} - \frac{1}{m_{e}} + n_{1}\bar{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} \right)$$
(15.146)

5 The total bond energy of the aromatic group  $E_D$  (Group) is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of  $c_4 E_{total}$  ( $c_4 AO / HO$ ) and  $c_5 E_{total}$  ( $c_5 AO / HO$ ):

$$E_{D}(Group) = - \begin{pmatrix} E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) \\ -31.63536831\ eV \\ -\left(c_{4}E_{initial}(AO/HO) + c_{5}E_{initial}(c_{5}AO/HO)\right) \end{pmatrix}$$
(15.147)

Since there are three electrons per aromatic bond,  $c_4$  is three times the number of aromatic 10 bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule  $(C_6H_6)$  section. The energy components of  $V_e$ ,  $V_p$ ,

15 T,  $V_m$ , and  $E_T$  are the same as those of the hydrogen carbide radical, except that  $E_T\left(C=C,2sp^3\right)=-1.13379~eV$  (Eq. (14.247)) is subtracted from  $E_T\left(CH\right)$  of Eq. (13.495) to match the energy of each C-H-bond MO to the decrease in the energy of the corresponding  $C2sp^3$  HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with  $E_T\left(atom-atom,msp^3.AO\right)=-1.13379~eV$ 

The total energy of the benzene C-H-bond MO,  $E_{T_{benzens}}\left(C-H\right)$ , given by Eq. (14.467) is the sum of  $0.5E_{T}\left(C=C,2sp^{3}\right)$ , the energy change of each  $C2sp^{3}$  shell per single bond due to the decrease in radius with the formation of the corresponding C=C-bond MO (Eq. (14.247)), and  $E_{T_{benzens}}\left(CH\right)$ , the  $\sigma$  MO contribution given by Eq. (14.441). In the corresponding 25 generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with  $f_{1}=1$  and  $E_{T}\left(atom-atom,msp^{3}.AO\right)=\frac{-1.13379\ eV}{2}$ . Thus, the energy

contribution to the single aromatic CH bond is one half that of the C=C double bond contribution. This matches the energies of the CH and C=C aromatic groups, conserves the electron number with the equivalent charge density as that of s=1 in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic C=C bonds to give CH groups creates unpaired electrons in these fragments that corresponds to  $c_3=1$  in Eq. (15.56) with  $E_{max}$  given by Eq. (15.58).

Each of the C-H bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each C-H bond,  $-E_{D_{benzene}}$  (12CH) (Eq. (14.477)), the total energy of the twelve electrons of the six C-H bonds of benzene,  $E_T(C_6H_6,C-H)$ , given by Eq. (14.494)

10 is

$$E_T(C_6H_6, C-H) = (6)(-E_{D_{backens}}(^{12}CH)) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV}$$
 (15.148)

The total bond dissociation energy of benzene,  $E_p(C_6H_6)$ , given by Eq. (14.495) is the negative

sum of 
$$E_T \left( C_6 H_6, C = C \right)$$
 (Eq. (14.493)) and  $E_T \left( C_6 H_6, C - H \right)$  (Eq. (14.494)):

$$E_{D}(C_{6}H_{6}) = -\left(E_{T}(C_{6}H_{6}, C = C) + E_{T}(C_{6}H_{6}, C - H)\right)$$

$$= -\left((-33.83284 \text{ eV}) + (-23.42724 \text{ eV})\right)$$

$$= 57.2601 \text{ eV}$$
(15.149)

15 Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule (C<sub>6</sub>H<sub>6</sub>) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 20 energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each  $E_D$  (Group) of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

Table 15.213. The symbols of functional groups of aromatics and hertocyclics.

Functional Group	. Group Symbol
CC (aromatic bond)	3e C=C
CH (aromatic)	- CH (i)

Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and

experimental values [1].

Parameter	C = C Group	<i>CH</i> Group
$a\left(a_{0}\right)$	1.47348	1.60061
$c'(a_0)$	1.31468	1.03299
Bond Length $2c'$ ( $\Box$ )	1.39140	1.09327
Exp. Bond Length	1.399 (benzene)	1.101 (benzene)
$b,c(a_0)$	0.66540	1.22265
e	0.89223	0.64537

5 Table 15.216. The energy parameters (eV) of functional groups of aromatics and heterocyclics.

Parameters	C = C Group	CH Group
$f_1$	0.75	1
$n_{\rm l}$	. 2	1
n <sub>2</sub>	0	0
n <sub>3</sub>	0	0
$C_1$	0.5	0.75
C <sub>2</sub>	0.85252	1
$c_{_{\mathrm{l}}}$	1	1
$c_2$	0.85252	0.91771
<i>c</i> <sub>3</sub>	0	1
$c_4$	3	. 1
$c_{\varsigma}$	0	1
$C_{lo}$	0.5	0.75
C <sub>20</sub>	0.85252	1
$V_{e}(eV)$	-101.12679	-37.10024
$V_{p}(eV)$	20.69825	13.17125
T(eV)	34.31559	11.58941
$V_{m}(eV)$	-17.15779	-5.79470
E(AO/HO)(eV)	0	-14.63489
$\Delta E_{H_2MO}$ (AO/HO) (eV)	0	-1.13379

$E_{T}$ (логно) (eV)	0	-13.50110
$E_T(H,MO)(eV)$	-63.27075	-31.63539
$E_T$ $(atom-atom, msp^3.AO)(eV)$	-2.26759	-0.56690
$E_{T}(MO)(eV)$	-65.53833	-32.20226
$\omega \left(10^{15}  rad  /  s\right)$	49.7272	26.4826
$E_{K}$ $(eV)$	32.73133	17.43132
$\vec{E}_{D}$ (eV)	-0.35806	-0.26130
$\overline{E}_{Kvtb}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364
$E_{mag}$ (eV)	0.14803	0.14803
$E_T(Group)(eV)$	-49.54347	-32.28590
$E_{initial}(4 \text{ AO/HO}) (eV)$	-14.63489	-14.63489
$E_{hittal}(s, AOIHO)(eV)$	0	-13.59844
$E_D$ (Group) $(eV)$	5.63881	3.90454

Table 15.215. The MO to HO intercept geometrical bond parameters of benzene.  $E_r$  is  $E_r(atom-atom,msp^3.AO)$ 

•	Atom	$E_T$	$E_T$	$E_T$	$E_T$	Final Total	, mina	rand
<del></del>		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy $C2sp^3$	(a <sub>0</sub> )	$\begin{pmatrix} a_0 \end{pmatrix}$
(CH)	2	-0.85035	-0.85035	-0.56690	0	(eV) -153.88327	0.91771	0.79597
3r 3r HCC	ຶ່	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597
,					•			

	Τ_	T
$\begin{pmatrix} d_2 \\ a_0 \end{pmatrix}$	0.21379	0.55533
$\begin{pmatrix} d_1 \\ (a_0 \end{pmatrix}$	1.24678	0.75935
$\begin{pmatrix} \theta_2 \\ 0 \end{pmatrix}$	38.84	58.98
(°)	105.58	45.76
(6)	74.42	134.24
$E\left(C2sp^{3}\right)$ (eV) Final	-16.90248	-16.90248
$E_{Conlord}(C2sp^3)(eV)$ Final	-17.09334	-17.09334
Bond	C-H(CH)	$C = HC_a = C$

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

Relative Error	0.00006
Experimental Total Bond Energy (eV)	57.26340
Calculated Total Bond Energy (eV)	57.26008
НЭ	9
3*C C=C	9
Name	Вепzепе
Formula	C,H,

Table 15.218. The bond angle parameters of benzene and experimental values [1].  $E_r$  is  $E_r$  (atom-atom,  $msp^3AO$ ).

$egin{array}{c cccc} C_2 & C_2 & C_1 & C_2 & C$	0.79232 0.79232 1 1
Atom 2 Hybridization Designation (Table 15.3.A)	-
Ecoulombic	-17.17218
Atom 1 Hybridization Designation (Table 15.3.A)	34
Ecoulombic	2.62936 2.62936 4.5585 -17.17218
$\begin{array}{c} 2c' \\ \text{Terminal} \\ \text{Atoms} \\ (a_0) \end{array}$	4.5585
2c' Bond 2 (a <sub>0</sub> )	2.62936
2c' Bond 1 (a <sub>0</sub> )	2.62936
Aions of Angle	ZCCC (aromatic)

	T	
$\operatorname{Exp.} \theta$ (c)	120 [50-52] (benzene)	120 [50-52] (benzene)
Саі. <i>ө</i> (e)	120,19	16,911
$\theta_{2}$ $(\circ)$		
φ <sub>1</sub>		120.19
9	i	
$E_{ m T}$ (eV)	-1.85836	-
<i>~</i> ~	0.79232	
$c_i$	1	
Atoms of Angle	ZCCC (aromatic)	ZCCH (aromatic)

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Table 1.1. The calculated and experimental total bond energies of n-alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
C₃H <sub>8</sub>	Propane	Energy (eV) 41,46896	Energy (eV) 41.434	-0.00085
C <sub>4</sub> H <sub>10</sub>	Butane	53.62666	53.61	-0.00036
C <sub>5</sub> H <sub>12</sub>	Pentane	65.78436	65.77	-0.00017
C <sub>6</sub> H <sub>14</sub>	Hexane	77.94206	77.93	-0.00019
C <sub>7</sub> H <sub>16</sub>	Heptane	90.09976	90.09	-0.00013
C <sub>8</sub> H <sub>18</sub>	Octane	102.25746	102.25	-0.00006
C <sub>9</sub> H <sub>20</sub>	Nonane	114.41516	114.40	-0.00012
$C_{10}H_{22}$	Decane	126,57286	126.57	-0.00003
C11H24	Undecane	138.73056	138.736	0.00004
C <sub>12</sub> H <sub>26</sub>	Dodecane	150.88826	150.88	-0.00008
C <sub>18</sub> H <sub>38</sub>	Octadecane	223.83446	223.85	0.00008

Table 1.2. The calculated and experimental total bond energies of branched alkanes using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Erro
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C <sub>4</sub> H <sub>10</sub>	Isobutane	53.69922	53.695	-0.00007
C5H12	Isopentane	65.85692	65.843	-0.00021
C5H12	Neopentane	65.86336	65.992	0.00195
$C_6H_{14}$	2-Methylpentane	78.01462	78.007	-0.00010
$C_6H_{14}$	3-Methylpentane	78.01462	77.979	-0.00046
C <sub>6</sub> H <sub>14</sub>	2,2-Dimethylbutane	78.02106	78.124	0.00132
C <sub>6</sub> H <sub>14</sub>	2,3-Dimethylbutane	77.99581	78.043	0.00061
C7H16	2-Methylhexane	90.17232	90.160	-0.00014
C <sub>7</sub> H <sub>16</sub>	3-Methylhexane	90.17232	90.127	-0.00051
C <sub>7</sub> H <sub>16</sub>	3-Ethylpentane	90.17232	90.108	-0.00072
C <sub>7</sub> H <sub>16</sub>	2,2-Dimethylpentane	90.17876	90.276	0.00107
C <sub>7</sub> H <sub>16</sub>	2,2,3-Trimethylbutane	90.22301	90.262	0.00044
C <sub>7</sub> H <sub>16</sub>	2,4-Dimethylpentane	90.24488	90.233	-0.00013
C <sub>7</sub> H <sub>16</sub>	3,3-Dimethylpentane	90.17876	90.227	0.00054
C <sub>8</sub> H <sub>18</sub>	2-Methylheptane	102.33002	102.322	-0.00008
C <sub>8</sub> H <sub>i8</sub>	3-Methylheptane	102.33002	102.293	-0.00036
C <sub>8</sub> H <sub>18</sub>	4-Methylheptane	102.33002	102.286	-0.00043
C <sub>8</sub> H <sub>18</sub>	3-Ethylhexane	102.30169	102.274	-0.00027
C <sub>8</sub> H <sub>18</sub>	2,2-Dimethylhexane	102.33646	102.417	0.00079
C <sub>8</sub> H <sub>18</sub>	2,3-Dimethylhexane	102.31121	102.306	-0.00005
C <sub>8</sub> H <sub>18</sub>	2,4-Dimethylhexane	102.40258	102.362	-0.00040
C <sub>8</sub> H <sub>18</sub>	2,5-Dimethylhexane	102.40258	102.396	-0.00006
C <sub>8</sub> H <sub>18</sub>	3,3-Dimethylhexane	102.33646	102.369	0.00032
C <sub>8</sub> H <sub>18</sub>	3,4-Dimethylhexane	102.31121	102.296	-0.00015
C <sub>8</sub> H <sub>18</sub>	3-Ethyl-2-methylpentane	102,31121	102,277	-0.00033
C <sub>8</sub> H <sub>18</sub>	3-Ethyl-3-methylpentane	102.33646	102.317	-0.00019
C <sub>8</sub> H <sub>18</sub>	2,2,3-Trimethylpentane	102.38071	102.370	-0.00010
C <sub>8</sub> H <sub>18</sub>	2,2,4-Trimethylpentane	102.40902	102.412	0.00003
C <sub>8</sub> H <sub>18</sub>	2,3,3-Trimethylpentane	102.38071	102.332	-0.00048
C <sub>8</sub> H <sub>18</sub>	2,3,4-Trimethylpentane	102.29240	102.342	0.00049
C <sub>8</sub> H <sub>18</sub>	2,2,3,3-Tetramethylbutane	102.41632	102.433	0.00016
C <sub>9</sub> H <sub>20</sub>	2,3,5-Trimethylhexane	114.54147	114.551	0.00008
C <sub>9</sub> H <sub>20</sub>	3,3-Diethylpentane	114.49416	114.455	-0.00034
C <sub>9</sub> H <sub>20</sub>	2,2,3,3-Tetramethylpentane	114.57402	114.494	-0.00070
C <sub>9</sub> H <sub>20</sub>	2,2,3,4-Tetramethylpentane	114.51960	114.492	-0.00024

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>9</sub> H <sub>20</sub>	2,2,4,4-Tetramethylpentane	114.57316	114.541	-0.00028
$C_9H_{20}$	2,3,3,4-Tetramethylpentane	114.58266	114.484	-0.00086
$C_{10}H_{22}$	2-Methylnonane	126.64542	126.680	0.00027
C <sub>10</sub> H <sub>22</sub>	5-Methylnonane	126.64542	126.663	0.00014

Table 1.3. The calculated and experimental total bond energies of alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>6</sub>	Propene	35.56033	35.63207	0.00201
C <sub>4</sub> H <sub>8</sub>	1-Butene	47.71803	47,78477	0.00140
C <sub>4</sub> H <sub>8</sub>	trans-2-Butene	47.93116	47.90395	-0.00057
C <sub>4</sub> H <sub>8</sub>	Isobutene	47.90314	47.96096	0.00121
C <sub>5</sub> H <sub>to</sub>	1-Pentene	59.87573	59.95094	0.00125
C <sub>5</sub> H <sub>10</sub>	trans-2-Pentene	60.08886	60.06287	-0.00043
C₅H <sub>10</sub>	2-Methyl-1-butene	60.06084	60.09707	0.00060
C <sub>5</sub> H <sub>10</sub>	2-Methyl-2-butene	60.21433	60.16444	-0.00083
C <sub>5</sub> H <sub>10</sub>	3-Methyl-1-butene	59.97662	60.01727	0.00068
C <sub>6</sub> H <sub>12</sub>	1-Hexene	72.03343	72.12954	0.00133
C <sub>6</sub> H <sub>12</sub>	trans-2-Hexene	72.24656	72.23733	-0.00013
C <sub>6</sub> H <sub>12</sub>	trans-3-Hexene	72.24656	72.24251	-0.00006
C <sub>6</sub> H <sub>12</sub>	2-Methyl-1-pentene	72.21854	72.29433	0.00105
C <sub>6</sub> H <sub>12</sub>	2-Methyl-2-pentene	72.37203	72.37206	0.00000
C <sub>6</sub> H <sub>12</sub>	3-Methyl-1-pentene	72.13432	72.19173	0.00080
C <sub>6</sub> H <sub>12</sub>	4-Methyl-1-pentene	72.10599	72.21038	0.00145
C <sub>6</sub> H <sub>12</sub>	3-Methyl-trans-2-pentene	72.37203	72.33268	-0.00054
C <sub>6</sub> H <sub>12</sub>	4-Methyl-trans-2-pentene	72.34745	72.31610	-0.00043
C <sub>6</sub> H <sub>12</sub>	2-Ethyl-1-butene	72.21854	72.25909	0.00056
C <sub>6</sub> H <sub>12</sub>	2,3-Dimethyl-1-butene	72.31943	72.32543	0.00008
C <sub>6</sub> H <sub>12</sub>	3,3-Dimethyl-1-butene	72.31796	72.30366	-0.00020
C <sub>6</sub> H <sub>12</sub>	2,3-Dimethyl-2-butene	72.49750	72.38450	-0.00156
C <sub>7</sub> H <sub>14</sub>	1-Heptene	84.19113	84.27084	0.00095
C7H14	5-Methyl-1-hexene	84.26369	84.30608	0.00050
C <sub>7</sub> H <sub>14</sub>	trans-3-Methyl-3-hexene	84.52973	84.42112	-0.00129
C <sub>7</sub> H <sub>14</sub>	2,4-Dimethyl-1-pentene	84.44880	84.49367	0.00053
C <sub>7</sub> H <sub>14</sub>	4,4-Dimethyl-1-pentene	84.27012	84.47087	0.00238
C <sub>7</sub> H <sub>14</sub>	2,4-Dimethyl-2-pentene	84.63062	84.54445	-0.00102 ·
C <sub>7</sub> H <sub>14</sub>	trans-4,4-Dimethyl-2-pentene	84.54076	84.54549	0.00006
C <sub>7</sub> H <sub>14</sub>	2-Ethyl-3-methyl-1-butene	84.47713	84.44910	-0.00033
C <sub>7</sub> H <sub>14</sub>	2,3,3-Trimethyl-1-butene	84.51274	84.51129	-0.00002
C <sub>8</sub> H <sub>16</sub>	1-Octene	96.34883	96.41421	0.00068
C <sub>8</sub> H <sub>16</sub>	trans-2,2-Dimethyl-3-hexene	96.69846	96.68782	-0.00011
C <sub>8</sub> H <sub>16</sub>	3-Ethyl-2-methyl-1-pentene	96.63483	96.61113	-0.00025
C <sub>8</sub> H <sub>16</sub>	2,4,4-Trimethyl-1-pentene	96.61293	96.71684	0.00107
C <sub>8</sub> H <sub>16</sub>	2,4,4-Trimethyl-2-pentene	96.67590	96.65880	-0.00018
$C_{10}H_{20}$	1-Decene	120.66423	120.74240	0.00065
$C_{12}H_{24}$	1-Dodecene	144.97963	145.07163	0.00063
$C_{16}H_{32}$	1-Hexadecene	193.61043	193.71766	0.00055

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Table 1.4. The calculated and experimental total bond energies of alkynes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>4</sub>	Propyne	29,42932	29,40432	-0.00085
C <sub>4</sub> H <sub>6</sub>	1-Butyne	41.58702	41.55495	-0.00077
C <sub>4</sub> H <sub>6</sub>	2-Butyne	41.72765	41,75705	0.00077
C <sub>9</sub> H <sub>16</sub>	1-Nonyne	102.37552	102.35367	-0.00021

Table 1.5. The calculated and experimental total bond energies of alkyl fluorides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CF <sub>4</sub>	Tetrafluoromethane	21.07992	21.016	-0.00303
CHF <sub>3</sub>	Trifluoromethane	 19.28398	19.362	0.00405
CH <sub>2</sub> F <sub>2</sub>	Difluoromethane	18.22209	18.280	0.00314
C <sub>3</sub> H <sub>7</sub> F	1-Fluoropropane	41.86745	41.885	0.00041
C <sub>3</sub> H <sub>7</sub> F	2-Fluoropropane	41.96834	41.963	-0.00012

Table 1.6. The calculated and experimental total bond energies of alkyl chlorides using closed-form equations having integers and fundamental constants only.

	• •			
Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CCI <sub>4</sub>	Tetrachloromethane	13.43181	13.448	0.00123
CHCl₃	Trichloromethane	14.49146	14.523	0.00217
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane	15.37248	15.450	0.00499
CH₃Cl	Chloromethane	16.26302	16.312	0.00299
C <sub>2</sub> H <sub>5</sub> Cl.	Chloroethane	28.61064	28.571	-0.00138
C₃H <sub>7</sub> Cl	1-Chloropropane	40.76834	40.723	-0.00112
C <sub>3</sub> H <sub>7</sub> Cl	2-Chloropropane	40.86923	40.858	-0.00028
C <sub>4</sub> H <sub>9</sub> Cl	1-Chlorobutane	52.92604	52.903	-0.00044
C <sub>4</sub> H <sub>9</sub> Cl	2-Chlorobutane	53.02693	52.972	-0.00104
C <sub>4</sub> H <sub>9</sub> Cl	1-Chloro-2-methylpropane	52.99860	52.953	-0.00085
C <sub>4</sub> H <sub>9</sub> Cl	2-Chloro-2-methylpropane	53.21057	53.191	-0.00037
C <sub>5</sub> H <sub>11</sub> Cl	1-Chloropentane	65.08374	65.061	-0.00034
C <sub>5</sub> H <sub>11</sub> Cl	1-Chloro-3-methylbutane	65.15630	65.111	-0.00069
C₅H <sub>11</sub> Cl	2-Chloro-2-methylbutane	65.36827	65.344	-0.00037
C <sub>5</sub> H <sub>11</sub> Cl	2-Chloro-3-methylbutane	65.16582	65.167	0.00002
C <sub>6</sub> H <sub>13</sub> Cl	2-Chlorohexane	77.34233	77.313	-0.00038
C <sub>8</sub> H <sub>17</sub> Cl	1-Chlorooctane	101.55684	101.564	0.00007
C12H25Cl	1-Chlorododecane	150.18764	150.202	0.00007
$C_{18}H_{37}CI$	1-Chlorooctadecane	223.13384	223.175	0.00018

Table 1.7. The calculated and experimental total bond energies of alkyl bromides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CBr <sub>4</sub>	Tetrabromomethane	11.25929	11.196	-0.00566
CHBr <sub>3</sub>	Tribromomethane	12.87698	12.919	0.00323
CH₃Br	Bromomethane	15.67551	15.732	0.00360
C <sub>2</sub> H <sub>5</sub> Br	Bromoethane	28.03939	27.953	-0.00308
C <sub>3</sub> H <sub>7</sub> Br	1-Bromopropane	40.19709	40.160	-0.00093
C <sub>3</sub> H <sub>7</sub> Br	2-Bromopropane	40.29798	40.288	-0.00024
$C_5H_{10}Br_2$	2,3-Dibromo-2-methylbutane	63.48143	63.477	-0.00007
C <sub>6</sub> H <sub>13</sub> Br	1-Bromohexane	76.67019	76.634	-0.00047
C <sub>7</sub> H <sub>15</sub> Br	1-Bromoheptane	88.82789	88.783	-0.00051
C <sub>8</sub> H <sub>17</sub> Br	1-Bromooctane	100.98559	100.952	-0.00033
C <sub>12</sub> H <sub>25</sub> Br	1-Bromododecane	149.61639	149.573	-0.00029
$C_{16}H_{33}Br$	1-Bromohexadecane	198.24719	198.192	-0.00028

Table 1.8. The calculated and experimental total bond energies of alkyl iodides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CHI <sub>3</sub>	Triiodomethane	10.35888	10.405	0.00444
$CH_2I_2$	Diiodomethane	12.94614	12.921	-0.00195
CH₃I	Iodomethane	15.20294	15.163	-0.00263
C <sub>2</sub> H <sub>5</sub> I	Iodoethane	27.36064	27.343	-0.00066
C <sub>3</sub> H <sub>7</sub> I	1-Iodopropane	39.51834	39.516	-0.00006
C <sub>3</sub> H <sub>7</sub> I	2-Iodopropane	39.61923	39.623	0.00009
C <sub>4</sub> H <sub>9</sub> I	2-Iodo-2-methylpropane	51.96057	51.899	-0.00119

Table 1.9. The calculated and experimental total bond energies of alkene halides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>3</sub> Cl	Chloroethene	22.46700	22.505	0.00170
C₃H₅Cl	2-Chloropropene	35.02984	35.05482	0.00071

Table 1.10. The calculated and experimental total bond energies of alcohols using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>4</sub> O	Methanol	21.11038	21.131	0.00097
C <sub>2</sub> H <sub>6</sub> O	Ethanol	33.40563	33.428	0.00066
C <sub>3</sub> H <sub>8</sub> O	1-Propanol	45.56333	45.584	0.00046
C <sub>3</sub> H <sub>8</sub> O	2-Propanol	45.72088	45.766	0.00098
$C_4H_{10}O$	1-Butanol	57.72103	57.736	0.00026
$C_4H_{10}O$	2-Butanol	57.87858	57.922	0.00074
C <sub>4</sub> H <sub>10</sub> O	2-Methyl-1-propananol	57.79359	57.828	0.00060
$C_4H_{10}O$	2-Methyl-2-propananol	58.15359	58.126	-0.00048
C <sub>5</sub> H <sub>12</sub> O	1-Pentanol	69,87873	69.887	0.00011

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	_
C5H12O	2-Pentanol	70.03628	70.057	0.00029
$C_5H_{12}O$	3-Pentanol	70.03628	70.097	0.00087
$C_5H_{12}O$	2-Methyl-1-butananol	69.95129	69.957	80000.0
$C_5H_{12}O$	3-Methyl-1-butananol	69.95129	69.950	-0.00002
$C_5H_{12}O$	2-Methyl-2-butananol	70.31129	70.246	-0.00092
C <sub>5</sub> H <sub>12</sub> O	3-Methyl-2-butananol	69.96081	70.083	0.00174
$C_6H_{14}O$	1-Hexanol	82.03643	82.054	0.00021
$C_6H_{14}O$	2-Hexanol	82.19398	82.236	0.00052
$C_7H_{16}O$	1-Heptanol	94.19413	94.214	0.00021
$C_8H_{18}O$	1-Octanol	106.35183	106.358	0.00006
$C_8H_{18}O$	2-Ethyl-1-hexananol	106.42439	106.459	0.00032
$C_9H_{20}O$	1-Nonanol	118.50953	118.521	0.00010
$C_{10}H_{22}O$	1-Decanol	130.66723	130.676	0.00007
$C_{12}H_{26}O$	1-Dodecanol	154.98263	154.984	0.00001
$C_{16}H_{34}O$	1-Hexadecanol	203.61343	203.603	-0.00005

Table 1.11. The calculated and experimental total bond energies of ethers using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond Total Bond	
		Energy (eV)	Energy (eV)	
C <sub>2</sub> H <sub>6</sub> O	Dimethyl ether	32.84496	32.902	0.00174
C <sub>3</sub> H <sub>8</sub> O	Ethyl methyl ether	45.19710	45.183	-0.00030
$C_4H_{10}O$	Diethyl ether	57.54924	57.500	-0.00086
$C_4H_{10}O$	Methyl propyl ether	57.35480	57.355	0.00000
$C_4H_{10}O$	Isopropyl methyl ether	57.45569	57.499	0.00075
C <sub>6</sub> H <sub>14</sub> O	Dipropyl ether	81.86464	<b>81.8</b> 17	-0.00059
$C_6H_{14}O$	Disopropyl ether	82.06642	82.088	0.00026
C <sub>6</sub> H <sub>14</sub> O	t-Butyl ethyl ether	82.10276	82.033	-0.00085
C <sub>7</sub> H <sub>16</sub> O	t-Butyl isopropyl ether	94.36135	94.438	0.00081
C <sub>8</sub> H <sub>18</sub> O	Dibutyl ether	106.18004	106.122	-0.00055
C <sub>8</sub> H <sub>18</sub> O	Di-sec-butyl ether	106.38182	106.410	0.00027
C <sub>8</sub> H <sub>18</sub> O	Di-t-butyl ether	106.36022	106.425	0.00061
C <sub>8</sub> H <sub>18</sub> O	t-Butyl isobutyl ether	106.65628	106.497	-0.00218

Table 1.12. The calculated and experimental total bond energies of 1° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>5</sub> N	Methylamine	23.88297	23.857	-0.00110
C <sub>2</sub> H <sub>7</sub> N	Ethylamine	36.04067	36.062	0.00060
C <sub>3</sub> H <sub>9</sub> N	Propylamine	48.19837	48.243	0.00092
$C_4H_{11}N$	Butylamine	60.35607	60.415	0.00098
$C_4H_{11}N$	sec-Butylamine	60.45696	60.547	0.00148
C <sub>4</sub> H <sub>11</sub> N	t-Butylamine	60.78863	60.717	-0.00118
$C_4H_{11}N$	Isobutylamine	60.42863	60.486	0.00094

Table 1.13. The calculated and experimental total bond energies of 2° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
		Energy (eV)	Energy (eV)	
C <sub>2</sub> H <sub>7</sub> N	Dimethylamine	35.76895	35.765	-0:00012
$C_4H_{11}N$	Diethylamine	60.22930	60.211	-0.00030
C <sub>6</sub> H <sub>15</sub> N	Dipropylamine	84.54470	84.558	0.00016
C <sub>6</sub> H <sub>15</sub> N	Diisopropylamine	84.74648	84.846	0.00117
C <sub>8</sub> H <sub>19</sub> N	Dibutylamine	108.86010	108.872	0.00011
C <sub>8</sub> H <sub>19</sub> N	Diisobutylamine	109.00522	109.106	0.00092

Table 1.14. The calculated and experimental total bond energies of 3° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>9</sub> N	Trimethylamine	47.83338	47.761	-0.00152
$C_6H_{15}N$	Triethylamine	84.30648	84.316	0.00012
$C_9H_{21}N$	Tripropylamine	120.77958	120.864	0.00070

Table 1.15. The calculated and experimental total bond energies of aldehydes using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	: •
		Energy (eV)	Energy (eV)	
CH <sub>2</sub> O	Formaldehyde	15.64628	15.655	0.00056
C <sub>2</sub> H <sub>4</sub> O	Acetaldehyde	28.18711	28.198	0.00039
$C_3H_6O$	Propanal	40.34481	40.345	0.00000
C <sub>4</sub> H <sub>8</sub> O	Butanal	52.50251	52.491	-0.00022
C₄H <sub>8</sub> O	Isobutanal	52.60340	52.604	0.00001
C <sub>5</sub> H <sub>10</sub> O	Pentanal	64.66021	64.682	0.00034
C <sub>7</sub> H <sub>14</sub> O	Heptanal	88.97561	88.942	-0.00038
C <sub>8</sub> H <sub>16</sub> O	Octanal	101.13331	101.179	0.00045
C <sub>8</sub> H <sub>16</sub> O	2-Ethylhexanal	101.20587	101.259	0.00053

Table 1.16. The calculated and experimental total bond energies of ketones using closed-form equations having integers and fundamental constants only.

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<del></del>		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	<b>Total Bond</b>	
		Energy (eV)	Energy (eV)	
C <sub>3</sub> H <sub>6</sub> O	Acetone	40.68472	40.672	-0.00031
C <sub>4</sub> H <sub>8</sub> O	2-Butanone	52.84242	52.84	-0.00005
C <sub>5</sub> H <sub>10</sub> O	2-Pentanone	65.00012	64.997	-0:00005
C <sub>5</sub> H <sub>10</sub> O	3-Pentanone	65.00012	64.997	-0.00005
C <sub>5</sub> H <sub>10</sub> O	3-Methyl-2-butanone	65.10101	65.036	-0.00099
C <sub>6</sub> H <sub>12</sub> O	2-Hexanone	77.15782	77.152	-0.00008
$C_6H_{12}O$	3-Hexanone	77.15782	77.138	-0.00025
C <sub>6</sub> H <sub>12</sub> O	2-Methyl-3-pentanone	77.25871	77.225	-0.00043
$C_6H_{12}O$	3,3-Dimethyl-2-butanone	77.29432	77.273	-0.00028
C <sub>2</sub> H <sub>14</sub> O	3-Heptanone	89.31552	89.287	-0.00032
C <sub>7</sub> H <sub>14</sub> O	4-Heptanone	89.31552	89.299	-0.00018
C <sub>7</sub> H <sub>14</sub> O	2,2-Dimethyl-3-pentanone	89.45202	89.458	0.00007

Formula	Name .	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>7</sub> H <sub>14</sub> O	2,4-Dimethyl-3-pentanone	89.51730	89.434	-0.00093
$C_8H_{16}O$	2,2,4-Trimethyl-3-pentanone	101.71061	101.660	-0.00049
C <sub>2</sub> H <sub>18</sub> O	2-Nonanone	113.63092	113.632	0.00001
C <sub>9</sub> H <sub>18</sub> O	5-Nonanone	113.63092	113.675	0.00039
C <sub>9</sub> H <sub>18</sub> O	2,6-Dimethyl-4-heptanone	113.77604	113.807	0.00027

Table 1.17. The calculated and experimental total bond energies of carboxylic acids using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CH <sub>2</sub> O <sub>2</sub>	Formic acid	21.01945	21.036	0.00079
$C_2H_4O_2$	Acetic acid	33.55916	33.537	-0.00066
$C_3H_6O_2$	Propanoic acid	45.71686	45.727	0.00022
$C_4H_8O_2$	Butanoic acid	57.87456	57.883	0.00015
$C_5H_{10}O_2$	Pentanoic acid	70.03226	69.995	-0.00053
$C_5H_{10}O_2$	3-Methylbutanoic acid	70.10482	70.183	0.00111
$C_5H_{10}O_2$	2,2-Dimethylpropanoic acid	70.31679	69.989	-0.00468
$C_6H_{12}O_2$	Hexanoic acid	82.18996	82.149	-0.00050
$C_7H_{14}O_2$	Heptanoic acid	94.34766	94.347	0.00000
$C_8H_{16}O_2$	Octanoic acid	106.50536	106.481	-0.00022
$C_9H_{18}O_2$	Nonanoic acid	118.66306	118.666	0.00003
$C_{10}H_{20}O_2$	Decanoic acid	130.82076	130.795	-0.00020
$C_{12}H_{24}O_2$	Dodecanoic acid	155.13616	155.176	0.00026
$C_{14}H_{28}O_2$	Tetradecanoic acid	179.45156	179.605	0.00085
$C_{15}H_{30}O_2$	Pentadecanoic acid	191.60926	191.606	-0.00002
$C_{16}H_{32}O_2$	Hexadecanoic acid	203.76696	203.948	0.00089
$C_{18}H_{36}O_2$	Stearic acid	228.08236	228.298	0.00094
$C_{20}H_{40}O_2$	Eicosanoic acid	252.39776	252.514	0.00046

Table 1.18. The calculated and experimental total bond energies of carboxylic acid esters using closed-form equations having integers and fundamental constants only.

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		Calculated	Experimental	Relative Error	
Formula	Name	Total Bond	Total Bond		
	·	Energy (eV)	Energy (eV)		
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Methyl formate	32.71076	32.762	0.00156	
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Methyl acetate	45.24849	45.288	0.00087	
$C_6H_{12}O_2$	Methyl pentanoate	81.72159	81.726	0.00005	
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Methyl hexanoate	93.87929	93.891	0.00012	
$C_8H_{16}O_2$	Methyl heptanoate	106.03699	106.079	0.00040	
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	Methyl octanoate	118.19469	118.217	0.00018	
$C_{10}H_{20}O_2$	Methyl nonanoate	130.35239	130.373	0.00016	
$C_{11}H_{22}O_2$	Methyl decanoate	142.51009	142.523	0.00009	
$C_{12}H_{24}O_2$	Methyl undecanoate	154.66779	154.677	0.00006	
$C_{13}H_{26}O_2$	Methyl dodecanoate	166.82549	166.842	0.00010	
$C_{14}H_{28}O_2$	Methyl tridecanoate	178.98319	179.000	0.00009	
$C_{15}H_{30}O_2$	Methyl tetradecanoate	191.14089	191.170	0.00015	
$C_{16}H_{32}O_2$	Methyl pentadecanoate	203.29859	203.356	0.00028	
$C_4H_8O_2$	Propyl formate	57.76366	57.746	-0.00030	
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Ethyl acetate	57.63888	57.548	-0.00157	
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Isopropyl acetate	69.89747	69.889	-0.00013	
$C_5H_{10}O_2$	Ethyl propanoate	69.79658	69.700	-0.00139	
$C_6H_{12}O_2$	Butyl acetate	81.95428	81.873	-0.00099	
$C_6H_{12}O_2$	t-Butyl acetate	82.23881	82.197	-0.00051	

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Methyl 2,2-dimethylpropanoate	82.00612	81.935	-0.00087
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Ethyl pentanoate	94.11198	94.033	-0.00084
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Ethyl 3-methylbutanoate	94.18454	94.252	0.00072
C7H14O2	Ethyl 2,2-dimethylpropanoate	94.39651	94.345	-0.00054
$C_8H_{16}O_2$	Isobutyl isobutanoate	106.44313	106.363	-0.00075
C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	Propyl pentanoate	106.26968	106.267	-0.00003
$C_8H_{16}O_2$	Isopropyl pentanoate	106.37057	106.384	0.00013
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	Butyl pentanoate	118.42738	118.489	0.00052
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	sec-Butyl pentanoate	118.52827	118.624	0.00081
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	Isobutyl pentanoate	118.49994	118.576	0.00064

Table 1.19. The calculated and experimental total bond energies of amides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
	4	Energy (eV)	Energy (eV)	
CH <sub>3</sub> NO	Formamide	23.68712	23.697	0.00041
C <sub>2</sub> H <sub>5</sub> NO	Acetamide	36.15222	36.103	-0.00135
C <sub>3</sub> H <sub>2</sub> NO	Propanamide	48.30992	48.264	-0.00094
C <sub>4</sub> H <sub>9</sub> NO	Butanamide	60.46762	60.449	-0.00030
C <sub>4</sub> H <sub>9</sub> NO	2-Methylpropanamide	60.51509	60.455	-0.00099
CHuNO	Pentanamide	72.62532	72.481	-0.00200
C <sub>5</sub> H <sub>11</sub> NO	2,2-Dimethylpropanamide	72.67890	72.718	0.00054
C <sub>6</sub> H <sub>13</sub> NO	Hexanamide	84.78302	84.780	-0.00004
C <sub>8</sub> H <sub>17</sub> NO	Octanamide	109.09842	109.071	-0.00025

Table 1.20. The calculated and experimental total bond energies of N-alkyl and N,N-dialkyl amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>7</sub> NO	N,N-Dimethylformamide	47.53142	47.574	0.00090
C₄H₀NO	N.N-Dimethylacetamide	59.91404	59.890	-0.00041
C <sub>6</sub> H <sub>13</sub> NO	N-Butylacetamide	84.63649	84.590	-0.00055

Table 1.21. The calculated and experimental total bond energies of urea using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>4</sub> N <sub>2</sub> O	Urea	31.35919	31.393	0.00108

Table 1.22. The calculated and experimental total bond energies of acid halide using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>3</sub> ClO	Acetyl chloride	28.02174	27.990	-0.00115

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Table 1.23. The calculated and experimental total bond energies of acid anhydrides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	Acetic anhydride	56.94096	56.948	0.00013
$C_6H_{10}O_3$	Propanoic anhydride	81.25636	81.401	0.00177

Table 1.24. The calculated and experimental total bond energies of nitriles using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
		Energy (eV)	Energy (eV)	
C <sub>2</sub> H <sub>3</sub> N	Acetonitrile	25.72060	25.77	0.00174
C <sub>3</sub> H <sub>5</sub> N	Propanenitrile	37.87830	37.94	0.00171
C <sub>4</sub> H <sub>7</sub> N	Butanenitrile	50.03600	50.08	0.00082
C <sub>4</sub> H <sub>7</sub> N	2-Methylpropanenitrile	50.13689	50.18	0.00092
C <sub>5</sub> H <sub>9</sub> N	Pentanenitrile	62.19370	62.26	0.00111
C <sub>5</sub> H <sub>9</sub> N	2,2-Dimethylpropanenitrile	62.47823	62.40	-0.00132
C <sub>7</sub> H <sub>13</sub> N	Heptanenitrile	86.50910	86.59	0.00089
C <sub>8</sub> H <sub>15</sub> N	Octanenitrile	98.66680	98.73	0.00069
$C_{10}H_{19}N$	Decanenitrile	122.98220	123.05	0.00057
$C_{14}H_{27}N$	Tetradecanenitrile	171.61300	171.70	0.00052

Table 1.25. The calculated and experimental total bond energies of thiols using closed-form equations having integers and fundamental constants only.

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		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	<b>Total Bond</b>	
		Energy (eV)	Energy (eV)	
HS	Hydrogen Sulfide	3.77430	3.653	-0.03320
H <sub>2</sub> S	Dihydrogen Sulfide	7.56058	7.605	0.00582
CH <sub>4</sub> S	Methanethiol	19.60264	19.575	-0.00141
C <sub>2</sub> H <sub>6</sub> S	Ethanethiol	31.76034	31.762	0.00005
C <sub>3</sub> H <sub>8</sub> S	1-Propanethiol	43.91804	43.933	0.00035
C <sub>3</sub> H <sub>8</sub> S	2-Propanethiol	44.01893	44.020	0.00003
C <sub>4</sub> H <sub>10</sub> S	1-Butanethiol	56.07574	56.089	0.00024
C₄H <sub>10</sub> S	2-Butanethiol	56.17663	56.181	0.00009
C <sub>4</sub> H <sub>10</sub> S	2-Methyl-1-propanethiol	56.14830	56.186	0.00066
C <sub>4</sub> H <sub>10</sub> S	2-Methyl-2-propanethiol	56.36027	56.313	-0.00084
C <sub>5</sub> H <sub>12</sub> S	2-Methyl-1-butanethiol	68.30600	68.314	0.00012
C <sub>5</sub> H <sub>12</sub> S	1-Pentanethiol	68.23344	68.264	0.00044
C <sub>5</sub> H <sub>12</sub> S	2-Methyl-2-butanethiol	68.51797	68.441	-0.00113
C <sub>5</sub> H <sub>12</sub> S	3-Methyl-2-butanethiol	68.31552	68.381	0.00095
C <sub>5</sub> H <sub>12</sub> S	2,2-Dimethyl-1-propanethiol	68.51797	68.461	-0.00084
C <sub>6</sub> H <sub>14</sub> S	1-Hexanethiol	80.39114	80.416	0.00031
C <sub>6</sub> H <sub>14</sub> S	2-Methyl-2-pentanethiol	80.67567	80.607	-0.00085
C <sub>6</sub> H <sub>14</sub> S	2,3-Dimethyl-2-butanethiol	80.71992	80.603	-0.00145
C7H16S	1-Heptanethiol	92.54884	92.570	0.00023
C <sub>10</sub> H <sub>22</sub> S	1-Decanethiol	129.02194	129.048	0.00020

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Table 1.26. The calculated and experimental total bond energies of sulfides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C <sub>2</sub> H <sub>6</sub> S	Dimethyl sulfide	31.65668	31.672	0.00048
C₃H <sub>8</sub> S	Ethyl methyl sulfide	43.81438	43.848	0.00078
$C_4H_{10}S$	Diethyl sulfide	55.97208	56.043	0.00126
C <sub>4</sub> H <sub>10</sub> S	Methyl propyl sulfide	55.97208	56.029	0.00102
C <sub>4</sub> H <sub>10</sub> S	Isopropyl methyl sulfide	56.07297	56.115	0.00075
C₅H <sub>12</sub> S	Butyl methyl sulfide	68.12978	68.185	0.00081
C <sub>5</sub> H <sub>12</sub> S	t-Butyl methyl sulfide	68.28245	68.381	0.00144
$C_5H_{12}S$	Ethyl propyl sulfide	68.12978	68.210	0.00117
C <sub>5</sub> H <sub>12</sub> S	Ethyl isopropyl sulfide	68.23067	68.350	0.00174
$C_6H_{14}S$	Diisopropyl sulfide	80.48926	80.542	0.00065
$C_6H_{14}S$	Butyl ethyl sulfide	80.28748	80.395	0.00133
$C_6H_{14}S$	Methyl pentyl sulfide	80.28748	80.332	0.00056
C <sub>8</sub> H <sub>18</sub> S .	Dibutyl sulfide	104.60288	104.701	0.00094
$C_8H_{18}S$	Di-sec-butyl sulfide	104.80466	104.701	-0.00099
C <sub>8</sub> H <sub>18</sub> S	Di-t-butyl sulfide	104.90822	104.920	0.00011
C <sub>8</sub> H <sub>18</sub> S	Diisobutyl sulfide	104.74800	104.834	0.00082
$C_{10}H_{22}S$	Ethyl propyl sulfide	128.91828	128.979	0.00047
$C_{10}H_{22}S$	Diisopentyl sulfide	129.06340	129.151	0.00047

Table 1.27. The calculated and experimental total bond energies of disulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	Dimethyl disulfide	Energy (eV) 34.48127	Energy (eV) 34.413	-0.00199
$C_4H_{10}S_2$	Diethyl disulfide	58.79667	58.873	0.00129
$C_6H_{14}S_2$	Dipropyl disulfide	83.11207	83.169	0.00068
$C_8H_{18}S_2$	Di-t-butyl disulfide	107.99653	107.919	-0.00072

Table 1.28. The calculated and experimental total bond energies of sulfoxides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> SO	Dimethyl sulfoxide	35.52450	35.435	-0.00253
C <sub>4</sub> H <sub>10</sub> SO	Diethyl sulfoxide	59.83990	59.891	0.00085
C <sub>6</sub> H <sub>14</sub> SO	Dipropyl sulfoxide	84.15530	84.294	0.00165

Table 1.29. The calculated and experimental total bond energies of sulfones using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_2$	Dimethyl sulfone	40.27588	40.316	0.00100

505 Table 1.30. The calculated and experimental total bond energies of sulfites using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> SO <sub>3</sub> C <sub>4</sub> H <sub>10</sub> SO <sub>3</sub>	Dimethyl sulfite Diethyl sulfite	43.95058	44.042	0.00207
$C_8H_{18}SO_3$	Dibutyl sulfite	68.54939 117.18019	68.648 117.191	0.00143 0.00009

Table 1.31. The calculated and experimental total bond energies of sulfates using closedform equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> SO <sub>4</sub>	Dimethyl sulfate	48.70617	48.734	0.00058
C <sub>4</sub> H <sub>10</sub> SO <sub>4</sub>	Diethyl sulfate	73.30077	73.346	0.00061
C <sub>6</sub> H <sub>14</sub> SO <sub>4</sub>	Dipropyl sulfate	97.61617	97.609	-0.00008

Table 1.32. The calculated and experimental total bond energies of nitro alkanes using closed-form equations having integers and fundamental constants only.

	•	Calculated	Experimental	Relative Error
<b>Formula</b>	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CH <sub>3</sub> NO <sub>2</sub>	Nitromethane	25.14934	25.107	-0.00168
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	Nitroethane	37,30704	37.292	-0.00040
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	1-Nitropropane	49.46474	49.451	-0.00028
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	2-Nitropropane	49.56563	49.602	0.00074
C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	1-Nitrobutane	61.62244	61.601	-0.00036
C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	2-Nitroisobutane	61.90697	: 61.945	0.00061
C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub>	1-Nitropentane	73.78014	73.759	-0.00028

Table 1.33. The calculated and experimental total bond energies of nitrite using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
		Energy (eV)	Energy (eV)	
CH <sub>3</sub> NO <sub>2</sub> M	lethyl nitrite	24.92328	24.955	0.00126

Table 1.34. The calculated and experimental total bond energies of nitrate using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> NO <sub>3</sub>	Methyl nitrate	28.18536	28.117	-0.00244
C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>	Ethyl nitrate	40.34306	40.396	0.00131
C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>	Propyl nitrate	52.50076	52.550	0.00093
C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>	Isopropyl nitrate	52.60165	52.725	0.00233

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Table 1.35. The calculated and experimental total bond energies of conjugated alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>5</sub> H <sub>8</sub>	Cyclopentene	54.83565	54.86117	0.00047
C <sub>4</sub> H <sub>6</sub>	1,3 Butadiene	42.09159	42.12705	0.00084
C <sub>5</sub> H <sub>8</sub>	1,3 Pentadiene	54.40776	54,42484	0.00034
C <sub>5</sub> H <sub>8</sub>	1,4 Pentadiene	54.03745	54.11806	0.00149
C <sub>5</sub> H <sub>6</sub>	1,3 Cyclopentadiene	49.27432	49.30294	0.00058

Table 1.36. The calculated and experimental total bond energies of aromatics and heterocyclic aromatics using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated	Experimental	Relative Erro
		Total Bond	Total Bond	
O IX		Energy (eV)	Energy (eV)	
C <sub>6</sub> H <sub>6</sub>	Benzene	57.26008	<b>57.26340</b>	0.00006
C <sub>6</sub> H <sub>5</sub> Cl	Chlorobenzene	56.55263	56.581	0.00051
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	m-dichlorobenzene	<b>55.84518</b>	55.852	0.00012
C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	1,2,3-trichlorobenzene	55.13773	55.077	-0.00111
C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	1,3,5-trichlorbenzene	55.29542	55.255	-0.00073
C <sub>6</sub> Cl <sub>6</sub>	Hexachlorobenzene	52.57130	. 52.477	-0.00179
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	Nitrobenzene	65.18754	65.217	0.00046
C <sub>7</sub> H <sub>8</sub>	Toluene	69.48425	69.546	0.00088
$C_7H_6O_2$	Benzoic acid	73.76938	73.762	-0.00009
C7H5ClO2	2-chlorobenzoic acid	73.06193	73.082	0.00027
C7H5ClO2	3-chlorobenzoic acid	73.26820	73.261	-0.00010
C <sub>7</sub> H <sub>5</sub> ClO <sub>2</sub>	4-chlorobenzoic acid	73.26820	73.247	-0.00028
C <sub>6</sub> H <sub>7</sub> N	Aniline	64.43373	64.374	-0.00093
$C_7H_9N$	2-methylaniline	76.62345	76.643	-0.00025
C <sub>7</sub> H <sub>9</sub> N	3-methylaniline	76.62345	76.661	0.00050
C <sub>7</sub> H <sub>9</sub> N	4-methylaniline	76.62345	76.654	0.00040
$C_6H_6N_2O_2$	2-nitroaniline	72.47476	72,424	-0.00070
$C_6H_6N_2O_2$	3-nitroaniline	72.47476	72.481	-0.00009
$C_6H_6N_2O_2$	4-nitroaniline	72.47476	72.476	-0.00002
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	Aniline-2-carboxylic acid	80.90857	80.941	0.00041
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	Aniline-3-carboxylic acid	80.90857	80.813	-0.00118
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	Aniline-4-carboxylic acid	80.90857	80.949	0.00050
C <sub>6</sub> H <sub>6</sub> O	Phenol	61.75817	61.704	-0.00087
$C_6H_4N_2O_5$	2,4-dinitrophenol	77,61308	77.642	0.00037
C <sub>6</sub> H <sub>8</sub> O	Anisole	73.39006	73.355	-0.00047
$C_{10}H_8$	Naphthalene	90.74658	90.79143	0.00049
C <sub>4</sub> H <sub>5</sub> N	Pyrrole	44.81090	44.785	-0.00057
C <sub>4</sub> H <sub>4</sub> O	Furan	41.67782	41.692	0.00033
C <sub>4</sub> H <sub>4</sub> S	Thiophene	40.42501	40.430	0.00033
C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	<b>Imidazole</b>	39.76343	39.74106	-0.00015
C <sub>5</sub> H <sub>5</sub> N	Pyridine	51.91802	51.87927	-0.00075
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrimidine	46.57597	46.51794	-0.00125
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrazine	46.57597	46.51380	0.00095
C <sub>9</sub> H <sub>7</sub> N	Quinoline	85.40453	85.48607	0.00093
C <sub>9</sub> H <sub>7</sub> N	Isoquinoline	85.40453	85.44358	0.00178
C <sub>8</sub> H <sub>7</sub> N	Indole	78.52215	78.514	-0.00040
C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>	Adenine	70.83735	70.79811	-0.00010

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#### Section V1

### Software Program

The present invention relates to a system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising: processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.

In one embodiment, for example, the system comprises five components: (1) the graphical user interface (GUI); (2) the routine for parsing between an input chemical structure or name and taking the input and activating a routine to call up the parts of the molecule (functional groups), which are used for determining the energies and structure to be rendered; (3) the functional-group data base that has an organization of the theoretical solutions; (4) the rendering engine, which calculates and enables manipulations of the image, such as a three-dimensional model in response to commands, as well as responds to commands for data parameters corresponding to the image such as bond energies and charge distribution and geometrical parameters; and (5) data transfer system for inputting numerical data into or out of the computational components and storage components of the main system. The system further comprises spreadsheets with solutions of the bond parameters with output in any standard spreadsheet format. The system also comprises a data-handling program to transfer data from the spreadsheets into the main program.

The output may be, for example, at least one of graphical, simulation, text, and numerical data. The output may be the calculation of at least one of: (1) a bond distance between two atoms; (2) a bond angle between three of the atoms; (3) a bond energy between two atoms; (4) orbital intercept distances and angles; and (5) charge-density functions of atomic, hybridized, and molecular orbitals, wherein the bond distance, bond angle, and bond energy are calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

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In other embodiments, the charge, current, energy, and geometrical parameters are output to be inputs to other programs that may be used in further applications. For example, the data of heats of formation may be input to another program to be used to predict stability (existence of compounds) equilibrium constants and to predict synthetic pathways. That is, a 5 novel composition of matter may be discovered by calculating at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of 10 atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The charge and current density functions may be used to predict the electric and magnetic fields of the species to determine other properties due to the interaction of the fields between species. These fields and the predictions of field interactions may be computed using Maxwell's equations. In one 15 embodiment, finite-element analysis is used to predict or calculate the interaction and resulting properties, such as the freezing point, boiling point, density, viscosity, and refractive index. Furthermore, the output data can be used to give thermodynamic, spectroscopic, and other properties, aid in drug design and other applications with or without direct visualization. Furthermore, the data can be input into other programs of the system, which calculate 20 thermodynamic and other properties, or performs a simulation, such as a chemical reaction or molecular dynamics.

The output data may be used to predict a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The novel property, for example, may be a new pharmaceutical use, or stability at room temperature of a novel arrangement of atoms or ions.

In one embodiment, the output device of the system is a display that displays at least one of visual or graphical media. The display may be at least one of static or dynamic. At least one of vibration, rotation, and translation may be displayed. The displayed information

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may be used for at least one of modeling reactivity, predicting physical properties, and aiding in drug and material design. The output device may be a monitor, video projector, printer, or one-, two- or three-dimensional rendering device. The displayed information may be used to model other molecules and provides utility to anticipate their reactivity and physical properties.

- 5 Additionally, data may be output and used in the same and additional applications as the rendered models and representations of the calculated physical solutions. The processing means of the system may be a general-purpose computer. The general-purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input
- 10 means. The input means may comprise a serial port, USB port, microphone input, camera input, keyboard or mouse. The processing means comprises a special purpose computer or other hardware system. The system may comprise computer program products such as computer readable medium having embodied therein program code means. The computer readable media may be any available media which can be accessed by a general purpose or
- 15 special purpose computer. The computer readable media may comprise, for example, at least one of RAM, ROM, EPROM, CD ROM, DVD or other optical disk storage, magnetic disk storage or other magnetic storage devices, or any other medium that can embody the desired program code means and which can be accessed by a general purpose or special purpose computer. The program code means may comprise executable instructions and data, which
- 20 cause a general purpose computer or special purpose computer to perform a certain function of a group of functions. Commercial examples of suitable program language includes, for example, C++, C, JAVA, FORTRAN, Python and Assembly Languages, programmed with an algorithm based on the physical solutions, and the computer may be a PC, mainframe, supercomputer, or cluster of computers. Commercial examples of suitable programs include,
- 25 for example, APIs like OpenGL, DirectX, FOX GUI toolkit, and Qt. This program may be developed to run on at least one of operating systems like Windows XP, Windows 2000, Windows Vista, MAC OS, MAC OS X, Linux, Unix, Irix and other Unix-type operating systems.

Millsian software is designed to render 3-D models of molecules, molecular ions,

molecular radicals, functional groups thereof, and related structure and property information
and produce useful data output and application of the parameters of these species, wherein the
nature of their bound electrons and chemical bonds are solved using Dr. Randell L. Mills'
Classical Quantum Mechanics theory described in the reference: R. L. Mills, "The Grand
Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional

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Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at http://www.blacklightpower.com/bookdownload.shtml, which is incorporated by this reference

Figure 76 will now be further explained:

in its entirety. Figure 76 provides a flow chart diagram, which is an example of a software

5 system that can be utilized for this purpose, which example is not intended to limit the scope of
the disclosed inventions. The main parts of this exemplary software system illustrated in

Start: A user can start the program by running an executable program file. That might be done, for example, by double clicking the program icon on a Windows-based operating system, or typing the name of the executable file on the command line and pressing the 'Enter' key on a Linux or Unix operating system. The program initially starts by reading data files located in specific directories. The names of those directories and locations are fixed according to the type and format of the data files.

Data files: There are two types of data files used in the software system: functional group data files and molecule data files. Functional group data files contain information about various functional groups. Functional groups are the basic bonding elements or units that each typically comprise an atom, or at least two atoms bound together as found within a molecule (e.g. -Cl, C=C, C=O, CH3). Functional groups typically dictate or define properties and structure of the molecule. Similar functional groups in different molecules typically react in similar ways when subjected to a particular set of reaction conditions. Molecule data files contain information about molecules, molecular ions, and molecular radicals. These data files are processed according to their file formats.

File formats: Millsian software employs two kinds of file formats for storing

25 information about the structure, energies and names of molecules and functional groups: rawdata format and hierarchical format. In a raw-data file, all information is stored as is, below
the header describing the type of information. As shown in the Table below, for example, the
names of the molecule or functional group are listed below the #NAMES header. The names
and positions of the atoms are listed below the #ATOMS header, and so on.

```
#NAMES
      CH3
      Alkane CH3
      #SMILES
 5
      C-
      #ATOMS
             C
                          0
                                 0
      1
      2
             Η
                   1.9775 -0.698 0
      3
             Η
                   -0.9888
                                 -0.698 1.712
      4
             Η
                   -0.9888
                                 -0.698 -1.712
10
      #AO
             1 1s
                   0.171
             1 2sp3 0.864 -1
      #BONDS
             12
                   1
                          1.649
      2
                          1.649
             13
                   1
      3
                          1.649
15
                   1
      #BONDAXES
             1
                   1
                         90
                                       0
      #DATA
      RCH bond angle: 109.44°
      CH bond length: 2.097 a
20
      HFORM: 12.492
```

Most of the functional groups files and some simple molecule files are stored in raw data format. The other file format used with the Millsian software system, the hierarchical file format, represents the information in a graph style, in which nodes are connected to other nodes through links. This format is designed to construct molecules by attaching different functional groups in a desired manner. Using this file format, the user can construct complex molecules built from solved functional groups.

For example, as shown in the Table below, the pentane data file includes a #GROUPS header below which is list all of the functional groups that form a part of the pentane molecule.

30 Under the #GROUP\_LINKS header is information about how these functional groups are connected to each other to construct pentane.

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					 <u> </u>	
#NAI	MES					
Penta	ne					-
#SMI	LES					
CCC	CC					
#GR0	OUPS					
1	C-					
2	-C-					
2 3	-C-					
4	-C-					
5	C-					
#CD4	OUP_L	NIVC				
#UK\		21	180			
2	1122		180	•		
3	32		180			
4 .	42	5 1	180			

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Processing data files: As further shown in the flow diagram of Figure 76 for the exemplary Millsian software system, the program first processes the functional group data file and constructs the functional-group objects, which are complete 3-D representations of the functional groups and their related information supplied in the corresponding file. These objects are then ready to be visually displayed through use of a molecule viewer. Next, the program processes the molecule data file. If the molecule date file is in raw-data format, then the program makes a molecule object directly from it. If the file is in hierarchical format, then the program calculates geometric parameters from listed functional groups. The program stores all functional-group objects and molecule objects using internal data structures.

Visualization/ User Interactions: As shown in Figures 77 and 78, the molecule viewer displays the functional-group objects and molecule objects and provides basic interaction capabilities with the displayed objects, such as rotating, scaling, and moving the objects. The molecule viewer also provides other visualization options, such as viewing molecules in wire frame mode, viewing coordinate axes, and changing of the transparency and lighting. The user, for example, can also select parts of a molecule for visualization, like a nucleus, atomic orbital, molecular orbital, or bond axis. The viewer also includes a drop down information window, which provides, for example, related information about molecules, such as bond angles, component functional groups, and total heat of formation. In one embodiment, a user can create new molecules by joining functional groups. For this purpose, the user can select a

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first functional group. Next, the user can select an open bond from the functional group where the user desires to attach another group. Next, the user can select another or the same functional group, followed by selecting an open bond from the other group. The user can join the two selected functional groups at the selected open bonds by clicking on 'Join Groups'.

5 This method of joining functional groups at open bonds can be repeated to form the desired molecule.

SMILES input: The Simplified Molecular Input Line Entry Specification or SMILES is a specification for unambiguously describing the structure of chemical molecules using short ASCII strings. Through the user interface, a user can enter SMILES to construct molecules, provided the new molecule comprises functional groups that are in the database. Once a SMILES is entered, a parser reads in and breaks it down into component functional groups. The software system then attaches the component functional groups to create the new molecule object, which can then be viewed using the molecule viewer.

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

## CONTINUOUS-CHAIN ALKANES $(C_n H_{2n+2}, n=3,4,5...\infty)$

The continuous-chain alkanes,  $C_n H_{2n+2}$ , are the homologous series comprising terminal methyl groups at each end of the chain with n-2 methylene  $(CH_2)$  groups in between:

$$CH_3(CH_2)_{n-2}CH_3$$
 (15.109)

- 5  $C_nH_{2n+2}$  can be solved using the same principles as those used to solve ethane and ethylene wherein the 2s and 2p shells of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three H AOs combine with three carbon  $2sp^3$  HOs and two H AOs combine with
- 10 two carbon  $2sp^3$  HOs to form each methyl and methylene group, respectively, where each bond comprises a  $H_2$ -type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The  $CH_3$  and  $CH_2$  groups bond by forming  $H_2$ -type MOs between the remaining  $C2sp^3$  HOs on the carbons such that each carbon forms four bonds involving its four  $C2sp^3$  HOs. For the alkyl C-C group,  $E_T(atom-atom, msp^3.AO)$  is
- 15  $-1.85836 \, eV$  where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the chain comprising methylene groups and terminal methyl groups.

The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of straight-chain alkanes are given in Tables 15.4,

- 20 15.5, and 15.6, respectively. The total energy of each straight-chain alkane given in Table 15.7 was calculated as the sum over the integer multiple of each  $E_D(G_{POUP})$  of Table 15.6 corresponding to functional-group composition of the molecule. The bond angle parameters of straight-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.8. In this angle table and those given in subsequent sections when  $c_2'$  is given as the ratio of two values of
- 25  $c_2$  designated to Atom 1 and Atom 2 and corresponding to  $E_{Coulombic}$  of Atom 1 and Atom 2,

respectively, then 
$$c_2' = \frac{c_2(Atom\ 2)}{c_2(Atom\ 1)}$$
.

Table 15.4. The geometrical bond parameters of straight-chain alkanes and experimental values [1].	netrical bond param	eters of straight-chair	n aikanes and experi
Parameter	CC. Group	C-H (CH <sub>3</sub> )	$C - H\left(CH_2\right)$ Group
$a\left( a_{0}\right)$	2.12499	1.64920	1,67122
c. (a,)	1.45744	1.04856	1.05553
Bond Length 2c' (A)	1.54280	1.10974	1.11713
Exp. Bond Length (A)	1.532 (propane) 1.531 (Dutane)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)
h,c (a,)	1.54616	1.27295	1.29569
ય	0.68600	0.63580	0.63159

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ole 15.5	I
Table 15.5	

7.00	7.7														
Pilog		E, (eV) Bond I	/r, (eV) Bond 2	E <sub>r</sub> (eV) Bond 3	<i>E<sub>r</sub></i> (eV) Bond 4	Final Total Energy C2xp³ (eV)	(a°)	(a) j'.	f((72/y²) (eV) Final	E(C.2xp²) (eV) Final	. ©	(°)	(°)	d, (a <sub>0</sub> )	(a <sub>0</sub> )
$C-H\left(CH_{3}\right)$	Ü	-0.92918	0	0	0	-152.54487	17716.0	0.86359	-15,75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
C-H (CH <sub>1</sub> )	ü	-0.92918	-0.92918	•	٥	-153.47406	0.91771	0.81549	-16.68412	-16,49325	68.47	111.53	35.84	1.35486	0.29333
H,C, -C,H,CH,	Ľ,	-0.92918	0	0	0	152,54487	17719.0	0,86359	-15.75493	-15.56407	53.82	116.18	30.08	1.83879	0,38106
H,C, -C,H,CH,	ິ່ນ	-0.02918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	26.41	(2.59	26.06	1.90890	0.45117
										***************************************					_

Table 15.6. The energy parameters (eV) of functional groups of straight-chain alkanes.

Table 15.6. The energy parameters Parameters	C-C	CH <sub>3</sub>	CH,
	Group	Group	Group
n	1	3	2
$n_2$	0	2	1
$n_3$	0	0	0
$C_1$	0.5	0.75	0.75
$C_2$	1	1	1
<u>c</u> 1	1	1	1
$c_2$	0.91771	0.91771	0.91771
<i>c</i> <sub>3</sub>	0	0	1
<i>c</i> <sub>4</sub>	2	1	1
$c_{5}$	0	3	2
C <sub>10</sub>	0.5	0.75	0.75
C <sub>20</sub>	1	1	1
$V_{o}(eV)$	-28.79214	-107.32728	-70.41425
$V_p(eV)$	9.33352	38.92728	25.78002
T(eV)	6.77464	32.53914	21.06675
$V_m(eV)$	-3.38732	-16.26957	-10.53337
E(AOIHO) $(eV)$	-15.56407	-15.56407	-15.56407
$\Delta E_{H_2MO}(AOIHO)$ (eV)	0	0	0
$E_r(AOIHO)$ (eV)	-15.56407	-15.56407	-15.56407
$E_{T}(H_{2}MO)$ (eV)	-31.63537	-67.69451	-49.66493
$E_T(atom-atom, msp^3.AO)$ (eV)	-1.85836	0	0
$E_r(MO)$ (eV)	-33.49373	-67.69450	-49.66493
$\omega \left(10^{15} \ rad \ / \ s\right)$	9.43699	24.9286	24.2751
$E_{\kappa}(eV)$	6.21159	16.40846	15.97831
$\overline{\overline{E}}_D$ (eV)	-0.16515	-0.25352	-0.25017
$\overline{\widetilde{E}}_{Krih}$ (eV)	0.12312 [2]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))
$\bar{E}_{osc}$ (eV)	-0.10359	-0.22757	-0.14502
$E_{mag}$ (eV)	0.14803	0.14803	0.14803
$E_{T}(Group) (eV)$	-33.59732	-67.92207	-49.80996
$E_{bnitial}(c_*AOIHO)$ (eV)	-14.63489	-14.63489	-14.63489
$E_{initial}(c_s AOIHO) (eV)$	0	-13.59844	-13.59844
$E_{D}(Group)$ (eV)	4.32754	12.49186	7.83016

١.

Table 15.7. The total bond energies of n-alkanes calculated using the functional group composition and the energies of Table 15.6 compared to the experimental values [3].

	Relative	Бтог		-0.00085	-0.00036	-0.00017	-0.00019	-0.00013	-0.00006	-0.00012	-0.00003	0.00004	-0.00008	0.00008
	Experimental	Total Bond	Energy (eV)	41.434	53.61	65.77	77.93	60.06	102.25	114.40	126.57	138.736	150.88	223.85
and chicking of it make the control of the chicking the c	Calculated	Total Bond Energy	(eV)	41.46896	53.62666	65.78436	77.94206	90.09976	102.25746	114,41516	126.57286	138.73056	150.88826	223.83446
Domino.	CH	•		_	7	"	4	5	9	7	00	٥	2	16
COLUMN TO	CH	<u>-</u>		7	7	7	7	7	7	~	7	7	7	7
TICLES OF	2-2			2	m	4	<b>V</b> 7	• •	7	∞	0	2	=	82
ADIC 13.7. THE LOTAL DOLLAR	Name	:		Propane	Butane	Pentane	Hexane	Hentane	Octane	Nonane	Decane	Undecane	Dodecane	Octadecane
Table 15.7.	Formula			3.5	Ę	C.H.	i i	H.S	Ę	H.J	H.	CHE	Co.F.	C L

Table 15.8. The bond angle parameters of straighte-chain alkanes and experimental values [1]. In the calculation of  $\theta$ , the parameters from the preceding angle were used.  $E_{\gamma}$  is  $E_{\gamma}(alom-atom,msp^{3}.AO)$ .

Exp. $\theta$	107 (propane)	112 (propane) 113.8 (butane)	111.0 (butane)			
हुं ७ €	108.44	110.49	110.49	109.50	109.44	109.44
θ <sub>1</sub> (°)						
(o)						
θ, (°)		69.51	15.69		70.56	70.56
$E_{r}$ (eV)	0	l		0		
ş	1.15796			1.15796		
5	0.75			0.75		
5. <b>5</b>	1					
ű	-			-		
G <sub>3</sub>	-			-		
C <sub>3</sub> Atom I	0.86359			0,86359		
Atom 2 Hybridization Designation (Table 18.3.A)	<b>3</b> E			æ		
Erwitesthi	I			н		
Atom I Hybridization Designation (Table 15.3.A)	,			7		
$\begin{pmatrix} 2c' & 2c' & 2c' & bord \\ bord & bord & Terminal \\ (a_b) & (a_b) & (a_b) \end{pmatrix}$ $\begin{pmatrix} 2c' & bc' \\ Aborns \\ (a_b) & (a_b) \end{pmatrix}$ Abor $\begin{pmatrix} 1c' & bc' \\ Aborns \\ (a_b) & (a_b) \end{pmatrix}$	15.75493			15.75493 C,		
2c' Turnina Atoms (a <sub>0</sub> )	3.4252			3.4252		Ī
2c' Bond 2 (a <sub>o</sub> )	2,110			1,0971		
2c' Bond ( (a <sub>b</sub> )	2,11106			2.09711 2.0971 3.4252 15.75493		
Atoms of Angle	Math.isra ∠HC_H 2.11106 2.1110 3.4252 15.75493	יט"ט"ס"	H,2,22	Methy!	7C,C,C,	17 000

## BRANCHED ALKANES ( $C_n H_{2n+2}$ , $n = 3,4,5...\infty$ )

The branched-chain alkanes,  $C_nH_{2n+2}$ , comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene (CH<sub>2</sub>), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene 5 functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-alkane groups are solved using the same principles as those 10 used to solve the methyl and methylene functional groups wherein the 2s and 2p AOs of each C hybridize to form a single 2sp3 shell as an energy minimum, and the sharing of electrons between two C2sp3 HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_r(atom-atom, msp^3.AO)$  of each C-C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is  $-1.85836 \, eV$  or  $-1.44915 \, eV$  based on 15 the energy match between the C2sp3 HOs corresponding to the energy contributions equivalent to those of methylene, -0.92918 eV (Eq. (14.513), or methyl, -0.72457 eV (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of branched-chain alkanes are given in Table 15.9. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. 20 (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkanes are given in Tables 15.10, 15.11, and 15.12, respectively. The total energy of each branched-chain alkane given in Table 15.13 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.12 corresponding to functional-group composition of the molecule. The bond angle parameters of branched-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.14.

Table 15.9. The symbols of functional groups of branched alkanes.

Functional Group	Group Symbol .
CH₃ group	$C-H(CH_3)$
CH₂ group	$C-H(CH_2)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

0.45117

1.90890

1.97162

1.83879

0.49298

1.97162

0.18708 0.29333 0.37326

1.23564 1.35486 1.42988

P. C.

	(£)	Group		2.10725	1.45164	1 63636	rrorr'		1332	(propane)	1,531	(butane)	1.52750	0.68888
	(e) (-')	Group		2.10725	1,45164	31363	50000		1.532	(propane)	 E	(butane)	1.52750	0.68888
	( <del>g</del> )	Group		2,12499	1.45744	90,73	09745		1.532	(bropane)	.53	(butane)	1.54616	0.68600
	( <u>c</u> )	Group		2,10725	1.45164		1.33033		1.532.	(propare)	1.531	(butane)	1.52750	0.68888
	(a) :)-:)	Gom G		2.12499	1,45744		087461		1.532	(propane)	1.531	(butane)	1.54616	0.68600
nerimental values 1	(a)	Group		2,12499	1.45744		1.54280		1.532	(propane)	1.531	(butane)	1.54616	0.68600
ched alkanes and ex	H)	Choup		1,67465	1.05661		1.11827				(isobutane)		1,29924	0.63095
d parameters of bran	( H.J) HJ		Group	1.67122	1.05553		1.11713		1.107	(C-H propane)	1117	(C - H butane)	1.29569	0.63159
Table 15.10. The geometrical bond parameters of branched alkanes and experimental values.	(80) 0 -0	(5,00) # = 1	Group	1.64920	1,04856		1.10974		1.107	geo	- 112	ane	1,27295	0,63580
Table 15.10.	Parameter			a (a,)	c. (a)	Bond	- Central	(4) 27	Evn Bond		196	<u> </u>	h,c (a,)	3

Table 15.11. The MO to HO intercept geometrical band parameters of branched-chain alkanes. R, R, R are H or alkyl groups. L, 13 L, arom. and L-arom. and L-arom. and	etrical bone	d parameters of b.	ranched-chain at	kanes. R.R., K	are Horalky	groups. Ar is	13. ( anom - an	om.msp All.					
Bond	Atom	13	E.	E.	177	Final Total	,	r Gard	(c.3rt.)	E(C2sp3)	ò	6	φ,
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Band 4	Energy (72yr)	(%)	(°°)	(eV) Final	(eV) Final	ေ	©	<b>O</b>
(H (r.H.)	ز	41,92918			e	-152.544K7	0.91771	0.46359	-15.75493	-15,56407	77.49	102.51	41,48
(H (cH,)	نا	4) 929/H	4192918	°	e	-153.47406	0,91771	0.81549	-16.68412	-16,49325	68.47	111.53	33.84
C-H (CH)	i.	-0,9291R	41.92918	A.92918	o	-154,40324	17716.0	0.77247	-17.61330	-17,42244	61.10	118.90	31.37
$H_3C_2H_4CH_3-$	ن	-0,0291K	С	0	0	-152.54487	1,7710,0	0,86359	-15.75493	-15,56407	63.82	116,18	30.08
$H_3C,C,H_3CH_3$	٤٠	41,92918	410201K	ø	0	-153,47406	0.91771	0.81549	-16,68412	-16.49325	36.41	123.59	30°9£
$R = H_2G_{\bullet}(H_1G_{\bullet} - R)HCH_1 - G_{\bullet}(G)$	ئ	41,9201K	41.92918	41.92918	Ð	-154.40324	0.01771	0,77247	-17.61330	-17,42344	48.30	02.161	21.30
$n - H_{\mathcal{L}}(R - H_{\mathcal{L}})C_{s}(R - H_{\mathcal{L}})CH_{s} - H_{\mathcal{L}}(R)$	ئ		-41,724.57	-0.724S7	181210-	-154,71860	17710.0	0.75889	-17.92866	-17.73779	48.21	131.79	21.74
$isoC_{i}C_{i}(H_{i}C_{i}-R)HCH_{i}-$	ن	40.9291H	41,92918	4) UZU ()-	D	rEEUF'F51-	177100	0.77247	-17.61330	-17.42244	48.30	131,70	21.90
$(R'_{*}, R'_{*}, H_{*}C_{*})C_{*}(R'_{*} - H_{*}C_{*})C_{*}$	U	10.T2M57	-0.T2M57	-0.72457	72M57.0-	-154.51300	1,7710,0	0,76763	-17.92866	-17.73779	50.02	129.96	22.66
$IuH(C,C_{\bullet}(H_{s}C_{s}-R)HCH_{s}-C)$ $(C-C,(0)$	ť	10,72457	81626'0-	-0.92918	<b>0</b> -	-154.19863	17160	0.78155	-17.40469	-17,21783	52.78	127.23	8
150C (R-H.C.)C.(R-H.C.)CH	ļ.,		277.02.0	121 02.0	0.37463	144 41100	111110	992920	-17.92866	9772771-	50.04	120.96	37.66

Parameters $CH$ , $CH$ , $C-H$ Group $Group$	CH, Group	CH <sub>1</sub> Group	dronb Gronb	C - C (a) Group	C-C (b) Group	C-C (c) Group	C – C (d) Group	C - C (e) Group	C~C (f) Group
'n,	3	7	1	1	1		-	1	-
$n_{j}$	2	1	0	0	0	0	0	0	٥
7,	0	0	0	0	0	٥	0	0	0
ប៊	0.75	0.75	0.75	0.5	6.5	0.5	0.5	0.5	0.5
ر.	1	1	1	1	1	_	1	1	1
ט	1	. 1	-	1	_	-	1	-	1
3	0.91771	0.91771	0.91771	0.91771	17716.0	17716.0	17710	0.91771	0.91771
່ປ	0	-	1	0	0	0	-	-	0
ថ	-		_	2	7	2	2	2	2
5	3	2	_	0	0	0	0	0	0
C <sub>1,0</sub>	0.75	0.75	0.75	0.5	6.0	6.5	6.5	0.5	5.0
<i>C</i> .,	-	-	1	1	1	1	1	I	-
V, (eV)	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (eV)	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(somo) (eV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta \mathcal{E}_{H_3M}(.mm)$ (eV)	0	0	0	0	0	0	0	0	0
$E_T(noin)$ (eV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\mathcal{E}_{r}(n_{z}\omega)$ (eV)	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom - atom, msp^3, AO)$ (eV)	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E_(1m) (aV)	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
w (1015 rad /s)	24.9286	24,2751	24.1759	9.43699	9.43699	15.4846	9,43699	9.55643	9.55643
$E_{\kappa}$ (eV)	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$ec{E}_n$ (eV)	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\tilde{E}_{Kab}$ (eV)	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0,09944 f51	0.12312	0.12312	0.12312
E (aV)	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Emery (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\gamma}(cinum)$ (BV)	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Ensted (r. NOTH) (eV)	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Eintlind (c. 1971110) (BV)	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{D}(i_{sour})$ (eV)	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Formula	Formula Name	HJ	מת	3	(a)	(4) 2-0		30	13 0	9,00	7		7
		· (5)	Š	3				(1)	(9)	(r)	Total Bond	Total Bond	ACCION CENTOR
7	Park state										Energy (eV)	Energy (eV)	
= :	teoontane	•	<b>-</b>	_	0	m	0		0	٥	53.69922	53,695	-0.00007
ב ב	Isopentane	-	_	_		•	0	0	0	0	65.83692	65.843	-0.00021
O.F.	Neopentano	4	0	0	0	0	4	0		-	9229859	64 900	0.00104
OH.	2-Methylpentane	m	7		7	•	•				20000		6,000
C.H.	3-Methylpentane	err	2	_	•	•					70,01402	/00'8/	0.00010
, i	2 2-Dimethylhumane	. ~		٠.	• -			> •	> •	<b>&gt;</b> .	78.01462	616.11	-0.00046
	2 2 Direct Alberta		- «		- (	> -	•		0	•	78,02106	78.124	0.00132
Z :	4.5-Umelaylouranc	•	3	7	0	4	0	_	0	0	77.99581	78.043	0.00061
CyHid	2-Methylhexane	m	6	<b></b>	m	m	0	0	0	-	55 177 37	9	A1000.0-
C,H,s	3-Methylhexane	m	•	_	~	•	0	-			CE CT. 100	20.00	1,000
CH.	3-Ethylpentane	m	m	-	-	- 647	. ~			• •	20.00	2.5	10000
CH.	2.2-Dimethylpentana	. ~		. ~			•	•	> <	> 0	70.11232	20.108	-0.00072
	2 2 Trimetal Incinit		4 6	٠ .	•••		•		9	0	90.17876	90.276	0.00107
<u>.</u> د د د	A C. S. Timinomy commis	n ·	۰ د	_ ,	•	7	m	0	-		90,22301	90,262	0.0004
ر با با ار با	2,4-Dimemyipentane	4	-	2	0	•	0	0	0	0	90.24488	90,233	-0.00013
ST.	3,3-Unnethylpentane	4	~	0	2	0	4	0	0	0	90.17876	90.227	0.00054
5.H.13	2-Methylheptane	m	4	_	₹	•	0	0	0		100 33000	103 323	80000
THE	3-Methylheptane	æ	4	_	4	٣	•	•	. 0		102 33002	102 203	90000
T.H.	4-Methylhoptane	m	4	_	4		•	c		• <	ניסטבר בטו	700.001	00000
g.Hg.	3-Ethylhexane	m	4	_	- 6-7	•				• <	102,33002	102.200	0.00043
T.	2,2-Dimethylliexane	4	3	0	-	-			• •	• •	777777	10771	0.00027
Į,	2,3-Dimethylhexane	•	7	7		•			• •	> <	10171	74-701	0.0009
H.	2.4-Dimethylhexane	-47	۰,		• -		> <	-	> 0		17116701	102.306	0.00005
H.	2.5-Dimethyllaxma			• ~			> <	> 0	> 0	۰ د	102.40238	102.352	-0.00040
H	3.3-Dimerly/thexane		. ~	4 6			> -	۰ د	<b>5</b>	۰ د	102.40258	102.396	-0.00006
: a	1 d-Directaille come	• •	۰.	> 0	<b>-</b> 1	٠.	•	0	0	0	102,33646	102,369	0.00032
	J. T. L.	•	7	7	7	4	•		0	0	102,31121	102,296	-0.00015
<u>.</u>	3-Einyl-4-inethylpentane	<b>.</b>	7	7	7	•	•	-	0	0	102,31,121	102.277	-0.00033
FFH 18	J-Ethyl-3-methylpentane	•	m	0	m	0	4	0	0	0	102 33646	102 317	610000
H.	2,2,3-Trimethy[pentane	ς,	_	_	_	2	m	0	0	_	102,38071	102 370	010000-
H.H.	2,2,4-Trimethylpentane	<b>~</b>		_	0	m	4	0	0	•	107 40907	102 412	0.0000
CaHis	2,3,3-Trimethylpentane	5		-	_	7	٣	0	•		100 38071	CEE 201	D 00048
E H	2,3,4-Trimethylpentane	S	0	•	C	•				٠.	9700	2077	0.000
C,H,I	2,2,3,3-Tetramethylbutane	9	0	•		. 0			· -	• •	04767701	267 001	0.00049
C,H,	2.3.5-Trimethylhexane	•	-			• •	• <	, <b>-</b>	٠.	•	75014.701	102.433	0.00016
C.F.	3.3-Diethylpentane	4	4	. =	> 4	٠.	> =		<b>-</b> 6	> 4	1474147	114,551	0.00008
C.H.	2.2.3.3-Tetramethylpentans	• •				• •			> -	> 0	114.49416	14.455	0.00034
. H.	2.2.3.4-Terramethylnentane		. c	, (	- <		<b>,</b>	, -	- ‹	۰ د	704/5-611	14.494	0.00070
CeH.	2.2.4.Terramerhyhenrane	• •	• -	• <	> <	n <	n 0	- «	> •	(	14,51960	114.492	0.00024
± ±	2 3 4-Termmerhalmentone		- c		> <		•	٠.		•	114,57316	14541	-0.00028
8 4	2. Mathidage and Committee of the Commit	o •	> \	٧.	۰ د	•	7 .	۰.	•	7	114.58266	114,484	-0.00086
2 : 2	Z-tyletuymomane	•	•	-	٥	•	0	0	•	0	126,64542	126.680	0.00027
. C.D.	Y-Methylnonane		•	_	•	,	•	•	•	•			

_	_			,								T	_
,	φ Ä	<u> </u>	107 (propana)	112 (propane) 113.8 (burane) 110.8 (isobutane)	111.0 (butane) 111.4 (isobutane)	}			110.8 (isobutane)		(isobutane)	111.4 (isobutane)	
!	हुं ५	• ©	108.44	110,49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	111.27	107.50
	9	©											
	9	©											_
1	θ,	<u> </u>		1569	69.51		70.56	70.56				_	72.50
ic used. Ly 13	Ē	(e <sub>\$</sub> )	0			0			-1.85836	0	0	-1.85836	
& aligic wo	ъ	_	1.15796			1.15796	, .		0.81549	1.04887	1.04887	1.04887	
picconi	v		0.75			0.75			1	0.75	0.75	0.75	
as moin un	ۍ		-	-		1		·	1	-	-	-	
c paramete	ָט		-			-			-	0.75	27.0	0.75	
n or o', u	ຜ	Atom 2	-			-			0.81549	17716.0	17716.0	0.91771	
e calculation	ŭ	Atom 1	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
and experimental values [1]. In the calculation of e., the parameters from the preceding aligne were used. Lt is try those construction of the parameters from the parameters and the parameters are preceding aligne were used.	Atom 2	Hybridization Designation	H			н			. 23	, ,	-	1	
experiment	E.	Atom 2	×			Ξ			-16.68412 C	-14.82575 C <sub>h</sub>	-14.82575 C <sub>o</sub>	-14.82575 C <sub>c</sub>	
Table 15.14. The bond angle parameters of branched-chain alkanes and	Atom 1	Hybridization Designation	7			,			25	۸.	sJ.	\$	
f branched-	3	Atom 1	-15.75493			-15.75493			-16.68412 C,	-15.55033 C <sub>n</sub>	-15.55033 C <sub>k</sub>	-15.55033 C,	
meters o	20,	Terwinal Atoms (a,)	1			3.4252			4.7958	4.1633	4.1633	4.7958	
ıngle para	20,	(a <sub>0</sub> )	211106			2.09711			2.91547	2,11323	2,09711	2.90327	
The bond	20.	Bond 1 (a <sub>0</sub> )	2.11106			2.09711			2.91547	2.91547	2.91547	2.90327	
Table 15.14.	Atoms of Angle		Methy bac	יב"כ"כ"	H'2"27	Methyl ZHC H	70.07	H 2 27	"ວ ¤	#° C' H	"2 on H"2"27	ັງ ພາ ່ວ່ວ ່ວ່າ	000/

## ALKENES $(C_n H_{2n}, n=3,4,5...\infty)$

The straight and branched-chain alkenes,  $C_n H_{2n}$ , comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, three distinct functional groups can be identified: C vinyl single bond to -C(C) = C, C vinyl single bond to -C(H) = C, and C vinyl single bond to  $-C(C) = CH_2$ . In addition,  $CH_2$  of the  $-C = CH_2$  moiety is an alkene functional group.

The alkyl portion of the alkene may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene (CH<sub>2</sub>), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds 15 can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkenes are equivalent to those in branched-chain alkanes. The solution of the functional groups comprises the hybridization of 20 the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two C2sp3 HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_r(atom-atom, msp^3.AO)$  of the C=Cbond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene,  $-2.26759 \, eV$ , given by Eq. (14.247).  $E_r \left(atom-atom, msp^3.AO\right)$  of each 25 C-C-bond MO in Eq. (15.52) is  $-1.85836 \, eV$  or  $-1.44915 \, eV$  based on the energy match between the C2sp3 HOs corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 \, eV$  (Eq. (14.513), or methyl,  $-0.72457 \, eV$  (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of alkenes are given in Table 15.15. The 30 geometrical (Eqs. (15.1-15.5) and (15.41)), intercept (Eqs. (15.71-15.78)), and energy (Eqs.

(15.6-15.11) and (15.17-15.56)) parameters of alkenes are given in Tables 15.16, 15.17, and 15.18, respectively. The total energy of each alkene given in Table 15.19 was calculated as the sum over the integer multiple of each  $E_D(G_{PRMP})$  of Table 15.18 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage 5, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(G_{PRMP})$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkenes determined using Eqs. (15.79-15.108) are given in Table 15.20.

of alkenes.	ð	٠ ١ ٢			(iii) 31-3 (iii) ii (iii) ii (iii)	$C = H \left( c u_1 \right) \left( u \right)$	$C \sim H \left( CH_3 \right)$	(a)	(") ("") (")	( - H	(a) (b) (c) (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	(a) 13 to 15		(a) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	(E) (F) (F) (F) (F) (F) (F) (F) (F) (F) (F		
Takle 14 14 The symbols of functional groups of alkenes.	Functional Group	CC double bond	C vinyl single band to -C(C)=C	C vinyl single band to -C(H)=C	O vinyl single band to -C(C))-CH2	CH2 alkenyl group		C.H. Broup	CH, alkyl group	#5	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to lso-C)	CC (t 10 t-C)	CC (t to iso-C)	

			_	_		_		_			_	_	_			
;	Оповр	2.10725		1.45164		1.53635		1.532	(propane)	(butane)		1.52750	0.68888			
2	Group	2.10725		1.45164		1.53635		1 533	(propane)	(butane)		1.52750	0.68888			
3	dronb	2 17400	,,,,,,	1,45744		1.54280			(propane)	(butane)		1.54616	O KRKIM	20000		
ָ ֖֖֖֖֭֓֞֝	Group	2 (100)	41012	1.45164		\$2925 1	200		(propane)	[.53] (butane)		1.52750	00000	0.00000		
٤	Group		2.12499	1 45744		00073	1.05		(propane)	1.531 (Autane)		1.54616		0.68600	!	
1700	Group		2.12499	1 167/14	pt/Ct/1		1,34260		1.532 (propane)	151	(ontenc)	1 54616		0.68600		
	Group		1.67465		1.03001		1.11827		1.122	(isobutane)		reapt .	1,4734	0.63095		
	$C-H$ ( $CH_1$ ) (ii)	Group	1.67122		1.05553		1.11713	1.107	H-2)	1.17	H-2)	Driming	1.29509	063159		
	C-H (CH <sub>3</sub> ) C		0.000	2000	1.04856		1.10974	1,107	H-2)	1,117	H-2)	butane)	1,27295	0 63680	0.03700	
	$-H(CH_1)$ (i)		1 64010	U.D#OILO	1.04566		1,10668		01:1	(2-methy (propers)	(1.3-butadlene)		1.26354	10000	0,03/30	
antal values	Orong C-C (iii)		0,0,0	2.04740	1.43087		1.51437			1,508			61797		0.69887	
THEOLOG PURGE	drond (i.) -(.)			2.04740	1 43087	inaria	1.51437			1,508	1		1 46.470	1.404.77	0.69887	
He de martine af Cally	C - C (i) Group			2,04740	1,43007	1.4300	1 51417	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,					0.777	1.404.37	0 49887	
	Table (5, 16. The geometrical point parameters of arterior $C = C$ $C$ $C$ $C$ $C$ $C$ $C$ $C$ $C$ $C$			1.47228		1,2600	1.94053	25045.	1.342	1.346	(2-bulene)	(1.3-bandiene)		0.75055	0.06030	
	Table 15.16. The Parameter			(0)		(a)	Bond Length	2¢, (7)	,	Length	\Z			h,c (a,)		

Bond	Atom	£,	E	. E <sub>7</sub>	E,	Final Total	,	, ,	E(C2p")	E(C2m)	ъ	θ,	ø	ď	d.
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	C2sp	(a)	હ	(eV) Final	Final	©	· ①	·©	(a)	(a)
$C_{\varepsilon}(H)C_{\varepsilon} = C_{\varepsilon}(H)C_{\varepsilon}$	Ů.	-1.1330	-0.92918	c	c	-153.67167	17716.0	0.80561	-14.88873	-16.69786	127.61	\$2.39	58.24	0.77492	0.49168
$C_{\bullet}(H)C_{\bullet}=C_{\bullet}H_{\bullet}$	٠	-1.13380	٠	٥	o	-152.74940	17116.0	. 25238'0	-15.95955	-15.76868	129.84	50.16	60.70	0.72540	0.54620
C,(C,)C,=C,H,C,		-1.1380	-0.72457	-0.72457	c	-154.19263	17716.0	0.78155	-17,40869	-17.21783	126.39	\$3.61	\$6.95	0.80289	0.46371
$R(C_{\mu}H_2 - C_{\mu}(C) = C$ $(C - C_{\mu}(i))$	Ů,	- 0.651,1-	-0.72457	-0.72457	c	-154,19863	1771	0.78155	-17,40869	-17,21713	60.88	119.12	27.79	L81127	0.31039
$(C-C, H_0, H_1 - C, C) = CH_1$ (C-C, 0) (C-C, 0) (C-C, 0) (C-C, 0)	ť	-0.72457	-0.9291R	. 9	c	-153,26945	17716.0	U82562	18647031	-1623864	DF 129	112.60	31.36	1,74221	031734
$R[C_1H_1-C_n(H)=C]$ (C-C(ii))	ن.	-1.13340	81626'0-	٥	0	-153.67866	177100	Q.R0561 .	-16.88873	-16.69786	64.37	115.43	29.79	1,77684	0.34596
$R(C,H_3-C,L(H)=C)$	Ů.	. 81626°0-	81626-0-	a	0	-153,47405	17712.0	QRISQ	-16,68411	-16.49325	66.59	114,01	30.58	1.76270	0,33183
C-H (CH,) (I)	.c.	-1.13380	6	С	c	-152.74949	ודדועם	0.85252	-15.959355	-13,76868	27.15	102.85	41.13	1.23.531	0.18965
С-н (СН,)	Ċ	81626°D-	. 0	O	0	-152,54487	17,16.0	0.86359	-15.75-193	-15,56407	77.49	102.51	41.48	1,23564	0.18708
$C = H\left(CH_{3}\right)$ (ii)	Ü	#1 <i>6</i> 26.0-	-0.92918	ø	u	-133,47406	17716.0	์ สาราชา	-16.68412	-16,49325	C#789	111.53	35.84	1.33486	0.29933
с – н (сн)	Ü	41,929,18	81626.0-	816Z630-	e	154 40324	17716.0	Q.77247	17.61330	-17.42244	61.10	118,90	31.37	1.42988	0.37326
$H_iC_iC_iH_iCH_i - (C-C_i(a))$	C,	-0.9201R	O	0	0	7 S2.54487	17710.0	05 EDM.D	-15.75493	-15.56407	63.82	116.18	30.08	(1887)	0.38106
H,C,C,H,CH, (C,-C_(n))	5	H1GZG'1>	816Z6 0-	U	8	153,47406	17714.0	0.81549	-16.68412	-16,49325	14.58	123.59	24,06	1.90830	0.45117
$R = H_2C_2G_4(H_2G_2 - R^2)HCH_1 - (C - C_1(b))$	<b>'</b> '	#16Z6')>	4.02018	40,92018	c	154.40324	17716.0	0,77247	-17.61330	-17,42244	48.30	07.161	21,50	1,97162	0.51388
$R = H_1C_*(R - H_1C_*)C_*(R - H_1C_*)CH_1 - (C - C_*(C))$	3	-(1.9291k	472457	-4172457	4,72457	.134,71860	17718.0	0.75889 .	-17.92KGG ·	-17.73779	18.21	131.79	21.74	1.95734	0.50570
$lan(C_{\kappa}(H_1C_{\kappa}-R))HCH_1-$ (C: -(: (d))	ئ	41.9291R	4162618	-0.9291R	8	MEDI+1431-	17716.0	0.77247	-17,61330	-(7,42244	48.30	07.161	21.50	1,97162	0.51311
$lartC_a(R^a - H_1C_a)C_a(R^a - H_1C_a)CH_1 - (C - C \cdot (e))$	ť	-0.72457	40 72457	-0.72457	-0.72457	-154.513999	0,91771	0,76765	-17.92KG6	677.71-	50.04	129.96	22.66	1.94462	0,49291
nent", C, (H, C, ~R') HCH, ~ (C - C' (f))	C.	0.72457	*16261>	H162611-	હ	-154.19863	(77)6'0	0,78155	-17,40869	-17.217#3	32.78	22.(2)	24,04	1.92443	0.47279
L(C-C'(R))	ڻ	15427.0-	181717-	-4,72457	-41,72457	.154,51399	1/1/16/0	0,76765	-17.92866	-17.7779	50,04	36.021	22.0%	I SHAKE	O.4920R

Table 15.18. The energy parameters (eV) of functional groups of alkenes	rs (eV) of func	tional groups	of alkenes.											0,0
Parameters	C=C Group	() Group	C-C (ii) Group	C-C (iii)	CH, (i)	C. C.	CH, (ii)	C - H Group	C-C (B)	C-C(b) Group	ල ර – ර Group	C-C (4)	Group	G-C (C) Group
7,	2	-	-	-	2	. 3	2	-	-	-	-	-	-	1
, r	0	0	0	0	-	2	_	٥	0	0	0	0	0	0
7	0	0	0	•	0	0	•	0	0	0	0	0	0	0
Ċ	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ပ်	17716.0	-	-	-	-		_			1	1	1	1	
	-	_	-	-	-	-	_	_	-	1	1	1	-	-
ď	17719.0	0.91771	. 17716.0	0.91771	. 17716.0	- 0.91771	0.91771	17716.0	0.91771	17716.0	0.91771	0.91771	0.91771	0.91771
,	0			-	-	0	-	-	0	0	0	1	-	0
, ,	4	2	2	2	-	1	-	_	.2	2	2	2	2	2
2	0	٥	0	0	7	3	2	_	0	0	0	0	0	0
	0.5	0.5	5.0	0.5	0.75	0.75	0.75	0.75	0.5	0.5	5.0	0.5	0.5	0.5
	0.91771	_	-	-	-	-	_	-	-	1	1	1	-	-
V (eV)	-102.08992	-30.19634	-30.19634	-30.19634	-72.03287	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	21.48386	9.50874	9.50874	9.50874	26.02344	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	34.67062	7,37432	7.37432	7,37432	21.95990	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (8V)	-17,33531	-3.68716	-3.68716	-3.68716	-10.97995	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3,38732	-3.45250	-3.45250
E(somo) (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
DE Line (some) (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
E. (LOINO) (8V)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{\mathbf{r}}(n_{i}, \mathbf{ro})$ (eV)	-63.27075	-31.63534	-31,63534	-31.63534	-49.66437	-67.69451	49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31,63537	-31.63535	-31.63535
$E_r(atom - atom, msp^3, AO)$ (eV)	-2.26759	-1.44915	-1.85836	-1.44915	0	0 :	0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
$E_r(\iota n)$ (eV)	-65.53833	-33.08452	-33.49373	-33,08452	-49.66493	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (1013 rad/s)	43.0680	15876.6	16.4962	9.97851	25.2077	24.9286	157.2.42	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
Er (eV)	28.34813	6.56803	10.85807	6.56803	16.59214	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	621159	6.29021	6.29021
Ē, (eV)	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Exist (eV)	0.17897	0.15895	0.09931	0.09931	0.35532 Eq.	0.35532 Eq. (13.458)	0.35532 Eq. (13,458)	0.35532 Eq. (13.458)	0.12312 [Z]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
Ē_ (eV)	-0.25568	-0.08827	-0.16869	-0.11809	-0.07727	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Em (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_r(true)$ (eV)	-66.04969	-33.17279	-33.66242	-33.20260	49.81948	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E man (c. 411111) (aV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Einter (c, with) (eV)	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	•	٥	0	0	٥
$E_D(i^{inqq})(gV)$	7.51014	3.75498	4.39264	3.78480	7.83968	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.19. The wal dond energies of alkenes calculated using the functional group composition and the energies of Table 15.18 compared to the experimental values [2]. The magnetic energy Eng that is subtracted from the verighted sum of the Eo (0-1) (04')

values base	values based on composition is given by (15.58).	m by (15.58).												ı					1
Formula	Name	ر <del>ء</del> ر	1.7.	زوز	١	CH. (i)	CH.	CH. (ii)	Œ	υ U	υ <u>-</u> υ	Ç	CIC	ט ט	(a) ∪~∪	Ä	Calculated	Experimental	Kelanve
		)	ε	€	•	,	•	•		3	2		€	e			Total Bond	Faretay (P.V.)	ETTO:
								ļ						-	6	6	35 56053	15 63207	0.00201
Į,	Propere	•	0	_				۰ د		٠.	> 0	•	•	•	, ,		47 31803	77 78477	000140
H.O	1-Butene	-	0	0	0	_	-	.,			<b>-</b>	<b>.</b>	<b>5</b> . (	، د	> <	> 0	47.71002	17 00206	0.000
C.H.	trans-2-Butene	_	٥	~	0	o.	7	•	7	0	>	<b>.</b>		٠.		۰ د	21000	20020	
<u> </u>	Techning	-	0	0	7	_	~	٥	•	0	0	•	0	0	0	3	41.50514	41.30030	0.00141
į	Partena	_	•	-	c		_	7	-		0	0	0	0	0	0	59.87573	29.9202	0,00123
5 C C	י-נימוחום							-	,	_	۰	0	•	0	۰	0	98880'09	. 60.06287	-0,00043
Ē	trans-2-renteno	_	٠ د	7	•	, .	٠,	٠.	. <	٠.			?	_	-	c	60.06084	60.09707	09000
Ę	2-Methyl-1-butene	-	5	>	7	-	7		٠.			•	• «	, (			55A1C 03	KN 16444	0.00092
H	2-Methyl-2-butene	_	-	_	0	•	m	0	-	0	-	>		۰ د	5 (	<b>.</b>	65-1430	00.1044	20000
į	2-Merhyl-1-hutere	_	0	_	0	-	m	0	7	0	7	0		0	•	Þ	29.97662	27.10.00	0,000
: C	- Common - C			-			_	*	-			0	0	0	0	0	72,03343	72,12954	0.00133
ξ. Έ	1-Hexene		<b>.</b>	- 1	۰ د	- •	- •	. •	٠,	٠.						c	72.74656	77.73733	-0.00013
Ę	trans-2-Hexene	_	0	7	>	>	7	7	4	7	> •	•		۰ ۱	•	•	2000	13636	90000
C.E.	mans-3-Hexene		0	7	•	0	7	7	7	7	>	-	÷	>	> -	> -	0.000	17.07	200000
	2 Marthall Commence	_		-	7	_	7	~	0	~	0	0	•	0	0	•	72.21834	17,29433	0.00.0
֓֞֞֜֞֝֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֡֓֓֓֓֓֓֓֡֓֞֓֓֡֡֓֡֓֡֓֡֓֡֓֡֓֡֡֡֓֓֡֓֡֡֓֡	הואברוואו-ו-מרוואו-ד		· •	, -				-	_		-	c	c	0	0	0	72,37203	72.37206	0000
Ĩ	2-Methyl-2-pentene	-	٧.	-	>	,	•	<b>-</b>	- 1		• •						40 13435	EV 101 CT	0.0000
Ä	3-Methyl-1-pentens	_	0		0	-	7		7		•	-	٠.	>	>	> -	1413434	211217	2000
1	4 Mathrill - nontrans	_	c	_	0	_	~	_	7	0	m	0	•	•	0	•	72,10399	86017.77	0.00145
CELLED	א-ואכיוואו-ז-מיומיום	•	•	•	,								. ,			,			
	3-Methyl-trans-2-	_	2		0	•	m	_	_		0	0	خ	0	0	9	12.57205	9075571	-0,00034
,	pentane		•																
	A Machini-Irane.					0		•	•	•	,	•	•	ć	•	•	37177	01915 62	-0 00043
C,H,	4-Mennying the	_	0	7	0	•	m	0	m		7	>	•	>	•	•		77.71	
,	pentene			•	•	•	•	•	,	,	<	•		•	•	c	72 21854	25900	0.00056
Ę.	2-Ethyl-1-butene	_	0	0	7	-	7	7	>	<b>.</b>	۰ د		•	•		•		5	00000
, H	2 3. Dimethyla Jahmens	_	0	•	ы	-	m	0	<del>-</del>	0	7	9	>	>	>	>	14.31945	14.34	2000
	1.2 Simeth I haden		•	-		_	141	0	_	٥	0	m	0	0	0	7	231796	72.30366	-0.00020
2	3.3-Umetry - 1-outens	<u>-</u> .	,	- (	•	٠,						•		•	0	•	72.49750	72,38450	-0.00156
H,	2,3-Dimethyl-2-butene		4	>	٠ د	> -	, .	, .	٠.	•							E4 101 13	24 77084	\$6000
Ž.	1-Heptene	_	0	_	0	-	-	4	-	•	<b>-</b>	٠ -		۰ د	•	•		00701	00000
±	S. Merhyl-1-hexens	-	0	_	0	_	~	~	cı		m	•	0			٠.	50507-60	97776	2000
;	Section of Property			_	-	•	ę.	7	_	~	•	0	0	0	0	0	84.52973	247112	-0.00129
ב כיי	יייייייייייייייייייייייייייייייייייייי		• •	٠.	• •			-	-	•	-	c	0	0	0	•	84.44880	84.49367	0.00053
Ē	2,4-Danethy-1-pentens		۰ د	٠.	4 9		۰ ۱					4		0	c	0	84 27012	84.47087	0.00238
C,H,	4,4-Dimethyl-1-pentent	_	0	-	>	_	n ·		٠.	•			•	• •		• •	29029 70	24 4444	50000
SH.	2.4-Dimethyl-2-pentene	_	~	_	0	0	4	•	7	9	7	>	>	•	>	,	THE PART OF THE PA		40100
•	rans-4 4-Dineshyd-2-	•	•	•	,	0	•		r		•	,,	ė	_	6	ç	84.54076	84.54.549	0.0000
C,H	- Curanita di Caran	-	0	7	>		•		,	>	•	3	•	,	,	•		!	
	pendie 7					-							•	•			-14-67	01 44010	20000
Į.	C-cliny-3-radiny-1-	-	0	0	7	•.	'n	<b>-</b>	-	-	7	0	ö	0	>	>	4.4//15	27.43.C	2,000
	butene																		
2	2,3,3-Trimethyl-I-	_	<	-	2	-,	4	0	٥	0	٥	m	0	0	٥	ņ	84.51274	84.51129	-0.00002
200	buteno	-	•	,								,	,	,	,	•	6047470	16777 30	0,0000
Ť	1-Octens	-	۰	0	-	<del>-</del>	-	'n	_	'n	0	,	o i	>	-	•	7074000	1711170	
:	trans-2,2-Directhyl-3-	-	•	r	•	0	٩	-	•	_	0	m	0	0	0	7	96.69846	96.68782	-0.0001
N. C.	hexens	-	>	4	>		,	-	•		•	,	;						
;	3-Edivi-2-methyl-1-	•	•	,	•	-	۳	·	-	,	,	0	¢	0	0	•	96.63483	51113	-0,00025
CH's	pentene	-	•	>	•		1	4	•	•		•	,		,				
;	2.4.4-Trimethyl-1-	٠	•	•	•	-	,	-	c		-	4	-	c	c	٥	96.61293	96.71684	0.00107
ź.	pentena	_	0	-	7		•	_	•		>	,	,	,	,	,			
;	2.4.4-Trimethyl-2-	•	•	•	•	0		c	_	c	c		0	0	•	7	96.67590	96.65880	810000
ř.	Denlene	-	7	-	>		•	•		•	•	,	,		. ,			***************************************	2,000
T.T.	1-December	_	0	-	0	-	-	7	_		0	•	•	0	•	0	120.00423	120.74240	0.0000
, H	I.Dodecene	_		-	0	-	_	٥	-	۵	0	٥	0	<b>.</b>	0	0	27963	145.07163	0.00063
	- Concense		, (		٠ .		_	<u></u>	_	2	0	0	0	0	0	٥	193.61043	193,71,766	0.00055
2	-100000000	-	>	-	>	-													

	Exp. θ (ο)			(1,3,5)exuriane CSCCCO (1,3,5)exuriane CSCCCO (1,3,5)exuriane CSCCCO (1,3,5)exuriane CSCC (1,3,5)exuriane (1,3,5)exuriane (1,3,5)exuriane (1,5,5)exuriane (1,5		118.5 (2-methylpropene)	121 (2-methylpropens)	(ourdand) .	112 (propane) 113.8 (butane) 110.8 (sobutane)	111.0 (butane) 111.4 (trobutane)				110.8 (isobutane)		111.4 (sobutane)	1[1.4 (isobutane)	
	(a)	118.36	113.84	123.46	118.19	116.31	121.85	103.44	110.49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	111.27	107.50
Ī	(C) %				123.46													
	ø (C)				118.36	•	16311											
	ø, ©								69.51	69.51		70.56	70.56					72.50
Er IS Er (wom - wom, mey .AU).	(eV)	0	-1.83836	-1.85836		0	g c	0			0			-1.85836	0	0	-1,85836	
mom	፞፞፞	1.07647	0.81549	a.81055		1.17300		1.15796			1.15796	·		0.81349	1.04887	1,04887	1,04887	
5 [ 2 1-	r.	0.75	1			0.75		0.73			0.75			_	0.75	0.75	0.75	
	ഗ്	-	,	<b>-</b> ,		-		1			-			•	1		1	
	ប	Q.75	1	-		-	,	1			-			-	0.75	0.75	0.75	
	G <sub>2</sub> Atlom 2	0,91771	0.81549	0.81549		-		-			-			0.81549	17716.0	0.91771	0.91771	
Juliana tra	Abum 1	0.85252	0.81549	0.80561		0.85252		0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
42	Atom 2 Hybridyzation Designation (Table 15.3.6)		. 34	77		æ		: н			н			. 25			<b>-</b>	
	E'cotante Atron 2	-14.82575 C,	2) -16,68411	-16.68411 C.		×		н			H			-16,68412	-14 82575 C,	-14.82575	-14.82575	
i i de amont motte.	Atom I Hybridizzuon Designation (Table 153.A)	6	**	æ				1			7			æ	~	\$	~	
mid experim	Erande Aken I	.15.95954	.16.63411	-16.88873 C,		-15,95955		-15.75493			-13.75493			-16.68412 ( }	-15,55033 C.	-15,55003 C.	-15,55033	
AUXCUCS	$\frac{2c'}{Torninal}$ Altein $(\alpha_0)$	4.2895	4.7958	4,7539		3.4756		3.4252			3.4252			4.7058	4,1633	4,1633	4.7958	
amerers or	2c' 	2.86175	2.86175	2.86175		2.04578		2,11106			2.09711			291547	21133	2.09711	2,90327	
a angre par	2c' Rund ( (a <sub>6</sub> )	6281172	2,198.2	2.53321		2.04578		2,11106			11607			2.91547	2.91547	2.91547	2.90327	
Table 15.20. The bond angle parameters of alkenes and experimental values [1]. In the calculation of o, the parameters from the presedung angle were used.	Assence of Angle	$C_{c}(H)C_{c}=C_{c}$	(''.'c''.'c'') ''.'c''.'c''	('ɔ'ɔ='ɔ) 'ɔ'ɔ'ɔ'	ZHC.C.	$\angle HC_{\mu}H$ $(H_{1}C_{\mu}=C_{1}C_{\nu})$	2C,C,H (H,C, = C,C,)	Mattylem ZHC, H	לנ"כ"נכ"	H", 7, 7, 7	Methy! ZHC,H	7,2,2,7	H",5",37	۳. ر. ۲۲. د. در د	Ας, ς, Η Ας, ς, Η	LC, C, H in C	2C,C,C,	"כנ'נ'נ'

ALKYNES 
$$(C_n H_{n-2}, n=3,4,5...\infty)$$

The straight and branched-chain alkynes,  $C_nH_{2n-2}$ , have at least one carbon-carbon triple bond comprising a functional group that is solved equivalently to the triple bond of acetylene. The triple bond may be bound to one or two carbon single bonds that substitute for the hydrogen atoms of acetylene. Based on the energy matching of the mutually bound C, these C-C-bond MOs are defined as primary and secondary C-C functional groups, respectively, that are unique to alkynes. In addition, the corresponding terminal CH of a primary alkyne comprises a functional group that is solved equivalently to the methylyne group of acetylene as given in the Acetylene Molecule section.

The alkyl portion of the alkyne may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkynes are equivalent to those in branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the 2s and 2p 20 AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_T(atom-atom,msp^3.AO)$  of the  $C \equiv C$ -bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of acetylene, -3.13026~eV, given by Eq. (14.342).  $E_T(atom-atom,msp^3.AO)$  of each -alkyl-bond MO in Eq. (15.52) is -1.85836~eV or -1.44915~eV based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of methylene, -0.92918~eV (Eq. (14.513), or methyl, -0.72457~eV (Eq. (14.151)), groups, respectively. For the C-C groups each, comprising a C single bond to  $C \equiv C$ ,  $E_T(atom-atom,msp^3.AO)$  is -0.72457~eV based on the energy match between the  $C2sp^3$  HOs for the mutually bound C of 30 the single and triple bonds. The parameter  $\omega$  of each group is matched for oscillation in the transition state based on the group being primary or secondary.

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The symbols of the functional groups of alkynes are given in Table 15.21. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkynes are given in Tables 15.22, 15.23, and 15.24, respectively. The total energy of each alkyne given in Table 15.25 is calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.24 corresponding to functional-group composition of the molecule. The bond angle parameters of alkynes determined using Eqs. (15.79-15.108) are given in Table 15.26. Each C of the  $C \equiv C$  group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene.

Table 15.21. The symbols of functional groups of alkynes.	s of alkynes.
Functional Group	Ordun Symbol
CC triple band	
C single bond to C et C (1°)	9.70
C single bond to C = C (2°)	
CH (terminal)	
CH, group	( H (CH.)
CH, group	(H, H, H, H)
CH (alkyl)	(i)
CC bond (n-C)	
CC bond (iso-C)	(E) (1)
CC bond (tert-C)	
CC (iso to iso-C)	
CC (tta t-C)	
CC (1 to iso-C)	(a) (j = )

	(B) .)~()	Croup	2 1075		1.45164	1 52,828	Project.		1.532	(propane)	1.53	(butane)		1	(52750	
	(a) (c)	dnoun	2.10725		1.45164	1.53635			1,532	(brobane)	1,531	(butane)		1 60060	06/751	-
	(g) .) - C	diodi	212499		1.43/44	1.54280			7237	(propane)	7	(pulane)		2000	010561	
	() () () () ()	dian	2.10725	77.77	1.43104	1.53635			1.532	(proparie)		(outpue)		1 52250	06120.	
	(a) (a) (b) (c) (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d		2.12499	1 45244	1.43 (ch.)	1.54280			7557	(pubbalie)	100	(atranta)		34616	2122	0.0000
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	Graup		2.12499	1 45744	1	1.54280			766.1	(augrand)	(Austral)	(animo)		1.54616		O COCO
1777	Orono		1.67465	1.05661		1.11827			- 23	(isohumana)	(			129924		0,63006
( )	ניש (כעי)	oner	1.67122	1.05553		1.11713	101	2 1	Dramme)	1117	H-31	hutane		1,29369		043150
1	(ca) 1-1	danis	1.54920	1.04836		1.10974	107	(C-H	Dropane)	1.117	(C-H	butane)		1.2725	20,000	0.05580
÷ •	Group	0,10	1.48719	0.99572		1.05383				(anatylene)			1 10462	20101	20000	0.000
(i) : [	Chorp	1 00100	1,718	1.41133		1.49369			1.450	(2,4-hexadiyne)			1,40567	1000	33802.0	0.000
(E)	Group	1 90186	20162	1.41133		1.49369			1,450				1 40557		0.70855	2000
ريان ديان	Group	1,28714		1.13452		1.20072	*0.	1.203	1 208	(2,4-benadiyme)			0.60793		0.88143	
		a (4,)		C (a)	Bond Length	2c' (A)		Exp. Bond	Cength	<u> </u>	•		h,c (a, )		23	
					_		۰.			_	_	٠.	_	4	-	ĸ

Bond	Atom	£,	. E.	£,	Er	Final Total	Ţ	Į.	E. (C2sp')	E(C2xp)	,0	<b>6</b>	œ" :	<b>b</b> - (	ď,
		(ev) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	C2sp cev.	(°)	(aº)	(eV) Final	(eV) Final		€	0	(0,)	(a,)
BC C - H		-1.5/513	٥	0	٥	-153,1MB2	14716.0	0.83008	-16.39088	-16,20003	96,99	89.01	48.71	0.98144	0.01428
		-1.56513	-0.36220	0	٥	-153.54311	17710,0	0.81213	-16.7317	-16.36231	137.17	42.13	65.25	0.53890	0.59562
		-1.56513	٥	С	o	-153.18082	17710,0	0.83008	-16.39088	-16.20002	19.781	42.09	66.24	0.51853	0,61599
C C. = C.H		0.36229	-0.92018		•	-152,90716	177100	0.84418	-16.11722	-15,92636	15.71	104.29	\$5.39	L61974	0.20841
C - H (CH <sub>3</sub> )	ن	#10Zu.n-	۵	c	٠	-152.54487	ועופס	0.86359	-15.75493	-15.56407	77.49	102.51	41,48	1,23564	0.18708
C - H (CH <sub>2</sub> )	U	MUZUU	81050.0-	۰	0	-153,47406	17716.0	0.81549	-16.68412	-16,49325	68.47	111.53	35.84	1.35416	0,20933
C-H (CH)	ပ	\$10Z615	*10,020,0	-0,9291K	0	154.40324	17710.0	0.77247	-17.6[330	-17,42244	61.10	118.90	31.37	1,42988	0,37326
H,C,C,H,CH,-	ن	#1026'0*	. 0	G	0	183-5251-	17710.0	0,16359	-13.75493	-15.36407	23.00	116.18	30.08	1.83879	901850
H,C,C,H,CH,	.,	816260-	#1026'a-	0	0	-153,47406	17716.0	0.81549	-16,68412	-16.49325	56.41	123.59	26.06	1.50830	0.45117
$R-H_1C_2C_3(H_1C_2-R^2)HCH_1-C_2C_3(R)$	ن	81026'0-	R1026'0-	816Z6'0*	0	1/2 EUP 1751	14116.0	D.77247	-17.61330	-17,42244	48.30	02.161	21.90	1.97142	0.51388
$R - H_1C_s(R^2 - H_1C_s)C_s(R^2 - H_1C_s)CH_1 - CC_s(C)$	ئ	81626°D-	-0.72457	721.0-	72M2T.0-	-134,71860	17710.0	0,75889	-11.92866	-17.73779	44.21	131.79	21.74	HE789.1	0.50570
$loc(C_s(H_1C_s-R)HCH_2-C_s(d))$	3	KIOZO O-	RI (SZK'O-	#10ZG'0-	O	-134,40324	177160	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1,97162	0.51388
nenC_(R'-H,C,)C;(R"-H,C,)CH, -	:*	.0.72457	-0.72457	-0.72457	-0.72457	-154,31399	14416.0	0,76763	17.92866	-17.73779	50.04	129.96	377.0	L.SAMG.	0.49298
$IRC_{\mathcal{C}_{i}}(H_{i}C_{i}-R^{i})HCH_{i}-C_{i}(f)$	ئ	TSNST. 0-	-0.92918	\$1626'O-	۵	-(54,19863	111160	0.78155	-17.40869	-17,21783	. 82.78	127,22	24.04	1,92443	0.47279
$LOC_{\mu}(R^{\mu}-H_{\mu}C_{\mu})C_{\mu}(R^{\mu}-H_{\mu}C_{\mu})CH_{\mu}-C_{\mu}CG_{\mu}$	3	4.72457	-0.72457	12421.0-	0.72457	-154.51399	17710.0	0.76765	-17.92866	-17.73779	. 30.04	129.96	22.66	1.94462	0.49298

Dommeter			0										
	Croup Group	C-C(E) Group	Group	Group	CH,	Gain	Group	C~C (a)	(a) 2+2 (b) 2+3	C-C (e) Group	C-C (d)	C-C (e) Group	C-C(f) Group
	3	-		_	m	7	_	-	=	-	_	_  _	-
	0	٥	0	0	2	-	0	0	٥	0	٥	٥	-
	0	0	0	0	0	٥	0	0	٥	0	0	0	-
	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	-	_	-	-	-	-	_	-	_	-	-	-	-
	-	-	-	-	-	_	-		-	-	_	-	
	0.91771	0.91771	0.91771	0.91771	17716.0	0.91771	17716.0	0.91771	0.91771	0.91771	17716.0	0.91771	17716.0
	2	-	1	0	0	-	-	0	0	0	_	-	0
	9	2	2		1	1	1	2	2	2	2	2	2
	٥	٥	0	-	3	2	1	0	0	0	0	0	0
	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	-		1	1	1	1	-	Т.	1	-	-	-	-
	-182.53826	-31.29307	-31.29307	-40.62396	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
	35.97770	9.64042	9.64042	13.66428	38.92728	25.78002	12.87680	9.33352	9.33352	9,37273	9.33352	9.37273	9.37273
	70.90876	7.85528	7.85528	13.65796	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
	-35.45438	-3.92764	-3.92764	-6.82898	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
	-16.20002	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.55407	-15 35946	-15.35946
$\Delta E_{\mu_1 \mu_2}(.\nu_1 m)$ (eV)	0	-0.72457	-0.72457	-3.130269	0	0	0	0	0 .	0	0	0	0
$E_r(Lono)$ (eV)	-16.20002	-13.91032	-13.91032	-11.50462	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
	-94.90616	-31.63533	-31.63533	-31.63532	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_r(atom - atom, msp^3.AO)$ (eV)	-3.13026	-0.72457	-0.72457	.0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
	-98.03637	-32.35994	-32.35994	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10 <sup>15</sup> rad / s)	20.0186	10.3988	17.5426	30.8370	24.9286	24.2751	24:1759	9.43699	.9.43699	15.4846	9.43699	9.55643	9.55643
	13.17659	6.84470	11.54682	20.29747	16.40846	15.97831	15.91299	621159	6,21159	10.19220	6.21159	6.29021	629021
	-0.23468	-0.16749	-0.21754	-0.28197	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
	0.27773 [9]	0.08989	0.08989 [9]	0.35532 Eq.	0.35532 Eq.	0.35532 Eq.	0.35532 Eq.	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
	-0.09581	-0.12255	-0.17260	-0.10430	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
	-98.02775	-32.48249	-32.53254	-31.73967	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Eneral (c viiino) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Eneral (c. 101110) (eV)	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	. 0	0	0	0	0
	10.21841	3.21271	3.26276	3.50634	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.24. The energy parameters (eV) of functional groups of alkynes.

	Experimental Relative Error	(•v)			41.75705 0.00070	١
	f) Calculated Total Bond Energy	.			. 41,72765	
mental values (2).	) C-C (q) C-C (e) C-C		0		000	
able 15.24 compared to the experir	(, -(; (a)     (-(; (b)     (-(; (c)	6	> c		0 0	
composition and the energies of	H <sub>3</sub> ('H <sub>1</sub> ('H (ii)	6		0 0	0 9	
ing the functional group	(C) (E) (C) (C) (C) (C) (C) (C) (C) (C) (C) (C		-	0	-	
of alkynes calculated us	: : : :	-	-	0	0	
25. The total bond energies	ניי	Propyne 1	1-Butyne	2-buryan	- Industria	
Table 15.		# :	ž	i a	01110	

	Esp ()		1	(buokne)	(propane) (13.8 (butane)	(isobutane)	(Buthre)	(isobutane)				110.8	(isobutane)		111.4	(Isobutane)	111.4	(emphapas)
	Cel. θ		3	108.44	110.49		110,49		109.50	13,8	100	109.4		2	111.27		111.27	_
	6.0																	
	9 O	_	_			_				1								
	0, ①	_	_	_	69.51		69.51		-	8		8	1					
om men 40)	E <sub>7</sub> (eV)			0					•			-1.85836	۰		0		-1.85836	٠
(atom - at	7		1 15706	1,13790					1.15796			0.81549	1.04887		1.04887		1.04887	
E. is E	4		1	;					0.75			-	27.0		0.75		0.75	
were used.	5		-	.					-			1	T-		-		_	
ding angle	٥		-									-	0.75		0.75		27.0	
m the prece	C <sub>1</sub>		-						-			0.81549	12711	Ī	17716.0	1	171160	1
ameters fro	Alona C		0.86359						0.86359			0.81549	0.87495	1	0.87495		0,87495	1
ition of $\theta$ , the par	Atom 2 Hybridization Designation	(1806 13.3.A)	I						H			22			-			
In the calcula	Economistic Atom 2		Ξ						=			-16.68412 C,	-14.82575 C.		ن وي	-14.82575	ن	
mental values [1].	Atom I Hybridization Designation	Victor and	r						,			22			•		'n	
and experir	E'i sudemale Asens I		-15.75493				-	1	-13.73493			-16.68412 C,	-15.55033 C.	.15 55033	Ľ,	-15.55033	౮	
falkynes	2c' Teminal Awras (a <sub>0</sub> )		3.4252					1	ŽŽ,			4.7958	4.1633	T	4.1633	+	4.7958	- 
ameters o	2c' Bond 2 (a <sub>0</sub> )		2.11106					2 00713				2.91547	2,11323	_	2.09711	-	7.00327	<b> </b>
d angle par	2¢' Band 1 (a <sub>0</sub> )		2,11106					1,100,1	_	1		2,91547	2.91547		2,91547	-	7.500.7	
Table 15.26. The bond angle parameters of alkynes and experimental values [1]. In the calculation of 6, the parameters from the preceding ungle were used. E. is E. (atom - atom men' AO)	officer of Angle	(C'C' = C'H)	Mathema ZHC, H		אניניני		H,0,0	Methy	200,00	7,1,1,1	4C,C,H	້ວ <sup>ສຸ</sup>	L,C,C,H	H,2,32	, C.	7,2,2,5 7,2,5	len C.	7C.C.C.

ALKYL FLUORIDES 
$$(C_n H_{2n+2-m} F_m, n=1,2,3,4,5... \infty m=1,2,3... \infty)$$

The branched-chain alkyl fluorides,  $C_n H_{2n+2-m} F_m$ , may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein 5 at least one H is replaced by a fluorine. The C-F bond comprises a functional group for each case of F replacing a H of methane in the series  $H_{4-m}C-F_m$ , m=1,2,3,4, and F replacing a H of an alkane. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-F functional groups comprises the hybridization of the 2s and 2p AQs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the F AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl fluorides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the F AO has an energy of  $E(F) = -17.42282 \, eV$ . To meet the equipotential condition of the union of the C-F  $H_2$ -20 type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the

$$c_2\left(C2sp^3HO \text{ to } F\right) = \frac{E\left(C, 2sp^3\right)}{E(F)}c_2\left(C2sp^3HO\right) = \frac{-14.63489 \text{ eV}}{-17.42282 \text{ eV}}\left(0.91771\right) = 0.77087 \quad (15.110)$$

C - F -bond MO given by Eqs. (15.68) and (15.70) is

 $E_T(atom-atom, msp^3.AO)$  of the C-F-bond MO in Eq. (15.52) based on the charge donation from F to the MO is determined by the linear combination that results in a energy that is a minimum which does not exceed the energy of the AO of the F atom to which it is energy matched.

The symbols of the functional groups of branched-chain alkyl fluorides are given in Table 15.27. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl fluorides are

given in Tables 15.28, 15.29, and 15.30, respectively. The total energy of each branched-chain alkyl fluoride given in Table 15.31 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.30 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). In the case of trifluoromethane,  $E_{mag}$  is positive since the term due to the fluorine atoms cancels that of the CH group. The C-C bonds to the CHF group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CF group (no H bonds to C) were each treated as a tert-butyl C-C.  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl fluorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.110) are given in Table 15.32.

Table 15.27. The symbols of functional groups of branched-chain alkyl fluorides.

Functional Group	Group Symbol
CF of $CF_m H_{4-m}$	C-F (i)
CF of $C_n H_{2n+2-m} F_m$	C-F (ii)
CH <sub>3</sub> group	$C-H(CH_3)$
CH₂ group	$C-H(CH_2)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

9,0	3	Group	2.10725	1.45164		1.53635		1.532	(propane)	1.53	(butane)	1.52750	0.68888
1	<u>و</u>	Granb	2.10725	1.45164		1.53635		1.532	(propane)	1.531	(butane)	1.52750	0.68838
	(B)	Group	212499	1.45744		1.54280		1.532	(propane)	1531	(buttane)	1.54616	0.68600
11.5	(9)	Oroup	2.101.2	1.45164		1.53635		1.532	(propare)	1531	(butane)	1.52750	0.68888
	(a)	Group	2,12499	1.45744		1.54280		1.532	(propane)	153	(butane)	1.54616	0.68600
	(E) (J-)	Group	2.12499	1.45744		1.54280		1,532	(propane)	155.	(butane)	1,54616	0.68600
		Group	1.67465	1.05661		1.11827			1.122	(isobutane)		1.29924	0.63095
ממושב ומויס מוויס מערכי וויס מוויס מוויס מוויס מוויס	( H.) H	Group	1.67122	1.05553		1,11713		1.107	(C - H propane)	6111	(C-H butane)	1.29569	0.63159
CRBITT CIPAL	(H.) H	Group	1.64920	1.04856		1.10974		1.107	(C-H propane)	1117	(C-H butane)	1.27295	0.63580
d parameters of cial.	C-F (ii)	Group	95157.1	1,31202		1,38858			1.382	Ē	•	1.11435	0.76219
able (3.26. The geometrical bond parameters of granding	0-6	Group	1.72139	1.31202		1.38858			1382	(ge	,	1,11435	0,76219
able 13.26.	Parameter		0 (0,)	c. (a,)	Bond	Length	(Y)	Cur Bond	Ap. Galle	1	₹)	h,c (a,)	

					١						7	$\overline{}$	٦					— <sub>T</sub>	7		$\neg$
1.8565   1.5865   1.5865   1.18074   1.1117   1.1117   1.5121   1.5221   1.5222						(a <sub>o</sub> )	0.13714	0.15714	0.09718	0.15714	0.18708	0.29933	92171.0	0.38106	0.45117	0.51388	0.50570	0.51388	0.49298	0.47279	0.49298
1.382						ط، (م)	1.15488	1.15488	1,21483	1.15488	1,23564	1.35486	1.42918	1.83879	1,90890	1.97162	1.95734	1.97162	1.94462	1.92443	1,94462
1,385   1,385   1,1974   1,1171   1,1187   1,520   1,520   1,523   1,533   1	1.53635	1,532 propane) 1,531 (butane)	1.52750	0.68888	;	(°)	47.86	47.16	45.11	67.86	41.48	35.84	31.37	30.08	26.06	21,90	21.74	21.90	22.66	24.04	99.77
1.3855   1.3858   1.1873   1.1173   1.1173   1.1173   1.1173   1.1273   1.1373   1.54290   1.5			_			(ο)	19.23	25.23	62.98	79.23	102.51	111.53	116.90	116.18	123.59	131.70	131.79	07.161	129.96	127.23	129.96
1.3855   1.38556   1.10774   1.11713   1.11827   1.54210   1.54220   1.55535   1.5553   1.5	1.5363	1.532 (propan 1.531 (butane	1.5275	0.6888		(•)	100'11	100.77	97.02	100.77	77.49	68.47	61.10	63.82	36.41	48.30	48.21	48.30	50.04	52.78	30.04
1.3858   1.3858   1.1074   1.1171   1.1187   1.5320	1.54280	1.532 (propane) 1.531 (buttane)	1.54616	0.68600		E(C2ερ²) (eV) Finai	-15.98435		-16,91353	·	-15.56407	-16,49325	-17.42244	-13.56407	-16.49325	-17,42244	617.67.71.	-17.42344	- 17.73779	CBT12.71-	97TET.71-
1.382   1.3826   1.1826   1.1074   1.11713   1.11827   1.5226   1.5226   1.5226   1.5221   1.5221   1.5221   1.5212   1.5212   1.5222   1.5226   1.5221   1.5212   1.5212   1.5222   1.5262   1.5222   1.5262   1.52222   1.52222   1.52222   1.5222   1.52222   1.52222   1.52222   1.52222   1.52222   1.52222	3635	532 ppane) 531 (tane)	2750	8888	,40).	Erect (eV) Final	-16.17521	-16.17521	-17,10440	-16.17521	-15.75493	-16.68412	-17.61330	-15.75493	-16,68412	-17,61330	-17.92866	-17.61330	-17.92866	-17.40869	-[7.92866
1.382   1.3826   1.1826   1.1074   1.11713   1.11827   1.5226   1.5226   1.5226   1.5221   1.5221   1.5221   1.5212   1.5212   1.5222   1.5226   1.5221   1.5212   1.5212   1.5222   1.5262   1.5222   1.5262   1.52222   1.52222   1.52222   1.5222   1.52222   1.52222   1.52222   1.52222   1.52222   1.52222	 		1.5	0.6	m – alam, msp	(a)	0,84115	0.84115	0,79546	0.84115	0.86359	0.81549	0.77247	0.86359	0,81549	0.77247	0.75889	0.77247	0.76763	0.78155	0.75765
1.3858   1.3858   1.1074   1.11713   1.11827   1.11827   (G-H propane)   (G-	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600		(°)	0.91771	0.78069	0.91771	0.78069	1771600	17716.0	17116.0	17710	17710.0	0.91771	0.91771	17710	17716.0	17710	17719.0
1.3858   1.3858   1.1074   1.1171   1.11827   1.11827   (G-H propane)   (G-H	1.54280	1,532 (propane) 1,531 (butane)	1,54616	0.68600	or alkyi groups.	Final Total Energy (.2.sp <sup>2</sup> (eV)	-15296515		.153,89433		-152,54487	-153.47406	-154,40324	-152.54487	-153.47406	-154,40324	-154,71860	-154.40324	-154.51399	-154,19863	-154,51399
Bond (a) (a) (b) (b) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	<u></u>		924	5601	R.R.R" are H	E <sub>T</sub> (eV) Bond 4	0	٥	8	0			٥	0	0	0	-0.72457	0	-0.724ST	ಕ	-0.72457
Bond   Langth   Lange   Lang	=		L	0.63	yl fluorides. //	6,7 (eV) Bond 3	•	_ 0	٥	۰	·	۰	-0.92918	0	0	-0.92918	-0.72457	-0.92918	-0.724ST	0.92918	-0.72457
Bond   Langth   1.3858   1.1874   1.1074     2c' (A)		ن ن	1	0.63159	othed-chain alk	(eV) Bond 2		٥	-0.92918			-0,92918	-0.92918		-0.92918	-0.92918	-0.72457	-0.92918	-0.72457	-0.92918	-0.72457
Bond   Langth   1.3858   1.3828   1.3828   2c (A)   2c	1.10974	1.107 C - H propane) 1.117 C - H butane)	1.27295	0.63580	parameters of bra	(eV) Band I	-1.34946	-1,34946	-134946	-134946	-0.92918	-0,92918	\$1626.0-	-0.92018	-0.92918	-0.92918	-0.92918	-0.93918	-6 72457	-0.72457	-0.72457
Bond   Langth   1.3858   1.3		382 (		6219	netrical bond	Atom	ن	2	ڻ	Ų.	i	i	ü	ن.	ਹ	Ľ,	ť	ย์	ڻ	ษ	ť
Band   Langth   1.38858   2e' (A)	ਜੁ 		٥	0.7	tercept geon												н.с.)сн. –		, KH, -		,)сн
Length  2e' (A)  Exp. Bond  Length  (A)  he (a,)  he (a,)  H <sub>1,1</sub> C <sub>1</sub> - F  H <sub>1</sub>	1.38858	1.382 (methyl fluoride	1,11435	0,76219	he MO to HO in										1.0	4,C, - R')HCH,	-H,C,)C,(R-	-R')HCH,-	C,)C,(R*-H;C	, - n') HCH <sub>2</sub> -	C,)C',(R"—H,C
	Length	Exp. Bond Length (A)	h,c (a,)	1	Table 15.29. 1	Bond	$H_{L-m}C_{\mu} - F_{\mu}$ (C, -F (i))	$H_{4-a}C_{a}-F_{a}$ (C <sub>a</sub> - F (i))	-H,C,C,F (C, -F (i))	-H <sub>3</sub> C <sub>3</sub> C <sub>3</sub> F (C <sub>1</sub> - F (ii))	C-H (CH,)	(-H (CH)	C-H (CH)	H,C,C,H,CH	H.C. C.H.CH	R-H;C;C;(1)	R-H;C, (R'-	150C,C,(H,C,	(C-C (e))	(C-C (A)	$IsnC_{\bullet}(R-H_{\bullet}G)$

Parameters	C-7	<b>\</b>	<i>(,H,</i> )	C#3	. H-0	(e) ()-()	(a) 2-2	(e) (c)—(c)	(g) ℃-℃	(e) ∵∵	(4) ンーン
	Group	Group	Group	Group	Group	drono	dnoso	dago	dneso	dinost	9 2 5
n	-	_	3	2	1	1	-		1	1	-
n,	0	0	3	1	. 0	0	0	0	0	٥	٥
n <sub>3</sub>	0	0	0	0	0	0	0	0	0	•	0
ני	5.0	0.5	0.75	6.75	0.75	0.5	50	5.0	50	0.5	20
	-	-	-		-	-	~	-	ı	-	1
6-	}	1	1	1	1	1	7	-	1	1	~
-6	0.77087	0.77087	17710.0	17716.0	17616.0	0.91771	17716.0	0.91771	17716.0	0.91771	17716.0
c,	0	0	0	1	-	0	0	0	1	-	0
c,	7	1	1		. 1	2	2	2	2	2	7
c,	0	0	3	2	1	0	O	0	0	D	0
	50	0.5	0.75	0.75	0.75	5.0	5.0	5.0	6.5	0.5	5.0
74		-	1	1	-	1	1	1	_	-	-
V, (eV)	-32.02108	-32,02108	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29,10112
V, (aV)	10.37015	10.37015	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	637273
" (eV)	4,10097	9.30097	32.53914	21.06675	10,48582	6.77464	6.77464	6,90500	6.77464	6,90300	6.90500
V_ (eV)	-4.65048	4.65048	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3,45250
E(.v. m) (eV)	-14.63489	-14,63489	-15.56407	-15.36407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15,35946
Alina (.v.a.) (eV)	0	0	0	0	0	0	0	0	0	0	0
$E_r(w m) (eV)$	-14.63489	-14,63489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
$\mathcal{E}_{\tau}(n_1\omega)$ (eV)	-31.63534	-31,63534	-67.69451	49.66493	-31.63533	-31,63537	-31,63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(alam - alam, mxp^t, AO)$ (4V)	-2.69892	-2.69892	0	0	. 0	-1.85836	-1.85836	-1,44915	-1,85836	-1,44915	-1,44915
$E_T(in)$ (cV)	-34.33429	-34,33429	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33,08452
w (10" rad)s)	24.8506	12.9435	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$\mathcal{E}_{L}$ (cV)	16.35707	8.51966	16.40846	15.97831	15.91299	621159	65112.9	10,19220	6.21159	6.29021	6.29021
$\vec{k}_{v}$ (cV)	-0.27472	-0.19826	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Him (UV)	0.13849 [10]	0,10911	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,35532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312 [2]	0.12312	0.12312
E (UV)	-0,20547	-0.14371	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E. (6V)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803
15 (may) (BV)	-34.53976	-34,47800	-67.92207	-49,80996.	-31.70737	-33.59732	-33,49373	-33,24376	-33.59732	-33.18712	-33.18712
Erang le, to uch (BV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489
mr (m m) (eV)	0	0	-13.59844	-13,59844	-13.59844	0	0	o	0	0	0
$E_D(a_{mp})$ (aV)	5.26998	5,20822	12.49186	7.83016	3,32601	432724	4.29921	3,97398	4.17951	3.62128	3,91734
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Table 15.31. The total bond energies of branched-chain alky! Aucrides calculated using the functional group composition and the energies of Table 15.30 compared to the experimental yalues [2]. The magnetic energy East that is subtracted from the

weighted s	weighted sum of the $E_1$ ( $\omega$ ) values based on composition is	values based on co	unposition is giv	given by (15.58).	,					•				•	•	
Formule	Name	C-F (i)	C-F (i) C-F (ii)	CH,	CH;	H.)	(c) (J-)	(e) ン-ン	ر-ر (و)	C-C (9)	C-C (d) C-C (e)	(J) D-0	13	Calculated Total Bond Energy (eV)	Experimental Total Bond Enemy (aV)	Experimental Relative Error Total Bond Enerty (eV)
£	Tetrafluoromethane	₹	٥	٥	٥	0	0	0	0	0		•	0	21.07992	21.016	-0,00003
Œ	Trifluoromethane	n	•	0	0	-	0	0	0	0	0	0	-	19,28398	19.362	0.00405
G.	Difluoromethene	•	6	•	-	٥	0	0	•	•	•	0	۰	18,37012	18.280	-0,00496
C,H,P	1-Fluoropropane	0	-	-	۲4	0	H	0	0	0	0	٥	·	41,86745	41.885	0.00043
られず	2-Fluorognosme	•	_	-	c	_	0	,	0	-	-	-	-	AT 96RTA	1 963	¢10010

· · · · · · · · · · · · · · · · · · ·	Exp. θ	108.8 (Augraforn)		(1,2-difluoroethane)	111.0 (1,1-diftuornethane)	(oundous)	112 (propane) 113.8 (bulane) 110.8 (Gobulane)	111.0 (butane) 111.4 (pobutane)				110.8 (isobutane)		111.4 (fsobutane)	111.4 (isobutane)	
	J = D	110.53	110.38	111.53	110.83	108.44	110,49	110.49	109.50	109.44	109.44	130.67	110.76	111.27	111.27	107,50
<del>.</del>	e. ©															
r,msp A	e_ ①	<u> </u>	ļ													
ını – aton	ø,⊙						18.69	69.31		70,S6	70.56					72.50
<ol> <li>E<sub>r</sub> is E<sub>r</sub> (atc</li> </ol>	<i>Β</i> <sub>7</sub> (eV)	-1.44915	0	-1,85836	۰	0			0			-1.85836	0	0	-1.85836	
e were use	٧	0.84115	17186.0	0.79318	188107	1.15796			96451'1			0.81549	1.04887	1.04887	1,04887	
ding angl	હ	-	0.75	-	0.73	0,75			87.0			1	0.75	0.75	0.75	
n the prese	ຽ	-	-	-	-	_			-			1	-	-	-	
meters from	ა	-	0.75	-	0.75	-			-				0.75	6.75	0.75	
of 8, the para	C <sub>3</sub> Alem 2	0.84115	0.78092 (Eq. (15.64))	0.77087 (Eq. (15.110))	12216'0	-			•			0.8 ( 549	12216'0	0,91771	14419.0	
the calculation	C3 Alere 1	0.84115	0.79546	0.81549	0.87495	0.86359			0.863.59			0.81549	0,87495	0.87495	0.87495	
Table 15.32. The bond angle parameters of tranched-chain alkyl fluorides and experimental values [1]. In the calculation of $ heta_i$ , the parameters from the preceding angle were used. E, is E, (aram – aram, msp*AO)	Alom 2 Hybridization Designation	(1)	Ŀ	Da.	<b>-</b> .							, 25	-	, <del>I</del> ;		
nd experime	Erapara Abara	-16.1731 F	-17.42282 F	-17.42383 F	-14.82575 C,	×			н			-16.68412 C.	-14.82 <i>575</i> (',	-14.82575 C.	-14,82575 C,	
alkyl fluorides a	Atom I Hybridization Designation	13	ĭ	22	\$	7			1			25	s	\$	s	
nched-chair	Eradent Akm 1	-16.1752  F	-17.10440	-16.68412 C.	-(5.5503) (C <sub>p</sub>	-(5.75493			-15,75493			-16 68412	-15.55@33 C.	-15.55033	.15.55033 C.	
eters of bra	Zc' Tornière Absent (O <sub>a</sub> )	43128	3,8987	4.5826	4.1633	3 4252			3.4252			4.7058	4.1633	4.1633	4.7958	
gle parant	2c' Rend 3 (a,)	2,62403	2,62403	2.62403	2,11106	211106			2.09711			191347	211323	2.09711	2.90327	
The bond an	2c'  bend   ( a,)	2.62403	211106	2.91,547	2,91547	2,11106			2.09711			291547	291547	2,91547	2,90327	
Table 15.32, 7	Aloris of Auglo	ZFC,F ((C, -F (i))	(C, - F (I))	2C,C,F (C, - F (f))	#,5,5,H (C, - F (f))	Methylau ZHC, H	35.07	Ĥ".)".)7	Methy!	ענ"ני"נ <u>'</u>	H", J", J7	".) <del>""</del> ".)".)7	,5 <del>4</del> 1,5,5 H	4C,C,H im C,	ZC,C,C,	13.33

ALKYL CHLORIDES  $(C_n H_{2n+2-m} Cl_m, n=1,2,3,4,5...\infty m=1,2,3...\infty)$ 

The branched-chain alkyl chlorides,  $C_nH_{2n+2-m}Cl_m$ , may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a chlorine. The C-Cl bond comprises a functional group for each case of Cl replacing a H of methane for the series  $H_{4-m}C-Cl_m$ , m=1,2,3, with the C-Cl bond of  $CCl_4$  comprising another functional group due to the limitation of the minimum energy of Cl matched to that of the  $C2sp^3$  HO. In addition, the C-Cl bond due to Cl replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-Cl functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the Cl AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl chlorides, the energy of chorine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq.

20 (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then,  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the Cl AO has an energy of  $E(Cl) = -12.96764 \, eV$ . To meet the equipotential condition of the union of the C - Cl  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the C - Cl-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ Cl\right) = \frac{E(Cl)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right) = \frac{-12.96764\ eV}{-14.63489\ eV}\left(0.91771\right) = 0.81317\ \ (15.110)$$

The valence energy of the carbon 2p is  $-11.2603 \, eV$  and that of the Cl AO is  $-12.96764 \, eV$ . The energy difference is more than that of  $2E_r \left(C-C,2sp^3\right)$  given by Eq. (14.151) for a single

bond. Thus,  $E_r(atom-atom,msp^3.AO)$  of the C-Cl-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is  $-1.44915\,eV$  based on the energy match between the  $C2sp^3$  HO and the Cl AO corresponding to the energy contributions equivalent to those of methyl groups,  $-0.72457\,eV$  (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl chlorides are given in Table 15.33. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl chlorides are given in Tables 15.34, 15.35, and 15.36, respectively. The total energy of each branched-chain alkyl chloride given in Table 15.37 was calculated as the sum over the integer multiple of each 10  $E_D(Group)$  of Table 15.36 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that was subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHCl group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CCl group (no H bonds to C) were each treated as a tert-butyl C-C.  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.38.

Table 15.33. The symbols of functional groups of branched-chain alkyl chlorides.

Functional Group	Group Symbol
CCl of CCl <sub>m</sub> H <sub>4-m</sub>	C-Cl (i)
CCl of CCl <sub>4</sub>	C-Cl (ii)
CCl of $C_n H_{2n+2-m} Cl_m$	C-Cl (iii)
CH <sub>3</sub> group	$C-H$ $(CH_3)$
CH₂ group	$C-H$ $(CH_2)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

200	(E)	dies	2.10725	1.45164	1.53635	1.532	(propere)	1.531	(butane)	1.52750	0 60000
	(e)	cion	2.10725	1.45164	1.53635	1.532	(propent)	1,531	(butane)	1,52750	000000
2,00	<del>()</del>	dnes	2.12499	1.45744	1.54280	1.532	(buobane)	[S]	(butane)	1,54616	0.69500
	(S)	Croup	2.10725	1.45164	1.53635	1,532	(propane)	153	(buttane)	1.52750	000070
	(a)	Group	2,12499	1,45744	1.54280	1.532	(propane)	<u>z</u>	(butane)	1.54616	007070
	(E)	Group	2,12499	1.45744	1.54280	1.532	(propane)	<u>s.</u>	(butane)	1.54616	00000
	#J	. Group	1.67465	1,05661	1.1827		1.122	. · (isobutano)		1,29924	20000
e i	C-# (CH.)	Oroup	1.67122	1.05553	1,11713	1.107	ပ္ပံ		(C-H butane)	1.29569	
likyl chlorades and experiment	C-H (CH.)	Oroup	1.64920	1.04856	1.10974	1,107	(C - H propane)	1.117	(C-H butene)	1.27295	
	(!!!) ひーン	Group	1,32621	1.69136	1,79005	1 803	(ethyl chlorids)	062.	4	1.59705	
Table 15.34. The peamerrical bond parameters of branched-chain	(ii) C-C	Grand	2.37026	1.70729	1.80692		1.767	(carbon totrachlorida)		1.64416	
The peometrical bond	() (J-C	Group	2,32621	1.69136	1,79005		1.785	(nachyl chloride)	,	1,59705	
Table 13.34.	Parameter		a (a,)	د. (۵۰)	Bond Cenguh 2c' (A)	Para Bank	Length Cons		<u> </u>	h,c (a,)	

Table 15.35. The MO to HO intercept geometrical bond parameters	errical bond	parameters of br	of branched-chain alkyl chlorides. R, R', Il" are H or alkyl groups.	kyl chlorides.	t, K', K' are H o	or alky! groups.	4 18 4	dom - alom, msp .All	-AC).						
Bond	Аюш	الب (eV) Bond ا	17- (aV) Bond 2	li, (eV) Bond 3	(eV) Bond 4	Final Total Energy ('24)	[] (a)	<u>, a</u>	Eratus (cV) Final	$E(C2\nu\rho')$ (eV) Final		, (°)	ø. ©	(a, )	(a) 1°
HC,(1, m=1,2,3,	ť	72.67.0+	a.		6	(8V) -(52.34026	17119.0	0.87495	:15.55033	-15.35046	89.69	11038	30,00	1,00500	0.104/2
$H_{\mu,\mu}(x, m=1,2,3, \dots = 1,2,3, \dots = 1,2,3,1,2,1,2,1,2,1,2,1,2,1,2,1,2,1,2,1,$	٦	rever,a-	6				1.05158	0.87495	-15.55033		57.89	11038	30.00	1,99599	O_JDMG1
C, C,((i))	ن	0.46459	-		c	-152.08028	17716.0	· 0.KB9R3	-15.2903-4	-13.09948	86,38	113.02	29.87	2.05530	0.34801
(;'C',	13	-0.46459		-	o		1.05158	0.88283	-15.2903-4		86'99	113.02	29.87	2.05530	0.34801
1) - "J", "L" - (J)	زرا	-0.72457	4107013		С	-153.26945	1,61771	0.12562	-16.47951	-16.28864	63.18	116.82	27.48	2,06384	0.37248
-H.J.J., -(1)	٦	-0.72457	۰	•	6		1,05151	0.87495	-13.53033		69.62	11031	30.50	1,99899	0.30463
C-H (CH,)	ن	-0.9201A			D	-152.54487	17716.0	0.86339	-15.75493	-15.56407	77.45	16251	41.48	1,23564	0.18708
(C-H (CH.)	į	40.92918	4/8180	-	G	-153,47406	17716,0	0,81349	-16,68412	-16,493325	68.47	111.33	35.84	1.35486	0,25733
C-H (CH)	ı	H\$ 6₹6'0-	-0.92918	-0.92018	c	-154.40324	17116.0	0.77247	0001971-	17,42244	61.10	118.90	31.37	1,42988	0.37326
H.f.;C,H.fCH; -	ڻ	#1929.G-		-	0	1875-5487	17716.0	0.86359	-13.75493	-15.56407	53.53	116.18	30.08	67.858.1	0.38106
H, C, L, M, C, M,	ئ	#1620.0-	-0.92918		0	-153.47406	17716.0	0.81549	-16.68413	-16.49325	56.41	123.59	26.06	1,90290	0.45117
R-H4', S, (H2C, -R) HCH; -	٠	\$10Z6'0-	40.92918	.0.0201R	0	PC225-1421-	0.91771	0.77247	00019'41-	HCZY'1)-	48.30	131.70	21.90	197162	0.51388
$R - H_1C_n(R^n - H_2C_n)C_n(R^n - H_2C_n)CH_2 - C(C_n)$	ڻ	A.92918	-0.72457	-0.72457	12457	0.154.718.00	0,91771	0,75889	99826'41-	-17.73779	48.21	131.79	21.74	1,95734	0.50570
$knC',C',(H,C,-R')HCH_2-$	ڻ	-0.92918	41,92918	-0.92918	o	PCEDP'HS1-	1411610	14£TT.0	-17,61330	-17,42344	41.30	131.70	21.50	1,97162	0.31388
(C-C (e))	ڻ	-0.72457	.0,72457	-D.72457	72457	154.31399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	37.00	1,94462	0.49798
(('-('(HJ', -K')HCHz-	ئ	-0.72457	-0.9291R	-0.9291N	ಕ	-154.19863	12160	0.78155	-17.40169	-17.21783	52.78	17,73	24.04	1,92443	0.47279
$ksot{(K'-H,C',J)}C_{*}(R^{*-}H_{2}C_{*})C'H_{3} - (C'-C',C)$	٠,	-0,72457	15921.0-	-0.72457	-0.72457	154.31399	0,91771	0.76765	-17,92866	-17.73779	\$0,04	129.96	22.66	1.94462	0.49798

Purameters C-CI	υ <del>-</del> υ	υ <u>-</u> -0	ひーひ	C.H.	Ë	H-D	(a) 2-2	(q) 2-2	(c)	(p) ::-::	(e) C-C (e)	C-C (B
	(i) Group	(ii) Quonb	(ii) (iii) Group	Group	Group	Group	Group	Group	Огощ	Group	Oronp	Group
п,	_	-	-	3	2	_	-	-	-		-	
n,	0	0	0	7	1	٥	0	٥	0	۰	0	0
n,	0	0	0	0	0	0	٥	0	0	0	•	
ť	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	20	20	0.5
.;	0.81317	0.81317	0.81317	-	-	-	_	-	-	-	-	-
ر.	-	-	-	-	-	-	_	-	-	_	-	-
ų.	-	-	1	12/11/0	0.91771	17716.0	17716.0	17716.0	0.91771	0.91771	0.91771	17160
	_	-	-	0	-	-	0	0	•	-	-	-
د.	2	7	2	-	1	-	2	7	2	7	7	7
ű	٥	0	0	٣	7	1	0	٥	٥	0	٥	٥
٤	0.5	0.5	0.5	0.75	52.0	0.75	0.5	0.5	0.5	20	0.5	0.5
. •	0.81317	0.81317	0.81317	-	-	-	_	-	_	_	-	-
V, (aV)	-29.68411	-28.95265	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29,10112
V, (aV)	8.04432	7.96922	8.04432	38,92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (aV)	9£08£'9	6.10748	6.38036	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (aV)	-3.19018	-3.05374	-3.19018	-16.26957	-10.53337	-5.24291	-3,38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
El.w no) (eV)	-14.63489	-14.63489	-14.63489	-15,36407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
ΔΕ <sub>η, νιο</sub> (.m m) (aV)	-1,44915	-0.92918	-1,44915	0	0	0	0	0	٥	0	0	0
F. (so so) (cV)	-13.18574	-13.70571	-13,18574	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15,35946
Er (u,in) (eV)	-31.63536	-31,63540	-31.63536	-67.69451	-49.66493	-31,63533	-31.63537	-31,63537	-31.63535	-31.63537	-31,63535	-31,63535
$E_{\tau}(atum - atom, mxp^3, AO)$ (cV)	-1.44915	-0.92918	-1.44915	0	0	0	95858.1-	-1.85836	-1.44915	-1.85836	-1.44915	-1,44915
E, (ud (cV)	-33.08452	-32,56455	-33.08452	-67.69450	-49.66493	-31.63537	-33,49373	-33,49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10 <sup>13</sup> red/s)	7.42995	7.22380	13.0612	24.9286	24.2751	24.1759	66927'6	9,43699	15.4846	9.43699	9,55643	9.55643
$E_{\kappa}$ (eV)	4.89052	4.75483	8,59708	16.40846	15.97831	15.91299	621159	6.21159	10.19220	6,21159	6.29021	6.29021
$E_{D}$ (eV)	-0.14475	-0.14048	-0,19191	-0.25352	-0.25017	-0.24966	-0.16515	-0,16515	-0.20896	-0.16515	-0.16416	-0.16416
Examp (all)	0.08059	0.08059	0,09113	0,35532 (Eq. (13,458))	0,35532 (Eq. (13,458))	0,35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312	0.12312	0.12512
E. (cV)	-0.10445	-0,10019	-0.14635	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Enter (eV)	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803
E, bound (cV)	-33.18897	-32.66473	-33.23086	-67.92207	-49.80996	-31.70737	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
Error (c, 10 m) (cV)	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489
Emmele, so mal (eV)	٥	0	٥	-13,59844	-13,59844	-13,59844	0	0	0	0	٥	
Entire) (eV)	3.77116	3.39496	3.96108	12.49186	7.83016	109ZE'E	4.32754	4.29921	3.97398	4.17951	3,62128	3.91734

	Relative	Emor			0.00123	0.00217	0.00499	0,00209	-0.00138	-0.00112	-0.00028	-0.00044	-0.00104	-0.00085	-0.00037	0.00034	-0.00069	-0.00037	0.00002	-0.00038	0.00007	0.0000
	Experiment	<b>'a</b>	Total Bond	Energy (eV)	13,448	14.52	15.450	16312	28,571	40,723	40,858	52,903	52,972	52.953	191.62	65.061	65.113	55.34 44.00	65.167	7,313	101.564	150,202
	Calminad	Total Bond	Energy (eV)	1	13.43.181	14.49146	15.37248	16,26302	28.61064	40.76834	40.86923	52,92604	52,02693	52.99860	53,21057	65.08379	65.15630	6536827	65.16582	77,34233	101,55684	150.87640
	A	ř			7	•	0	0	0	0	0	0	0	0	7	٥	0	<del>.</del>	0	٥	•	۰
	9				0	•	0	0	0	0	0	0	0	0	0	0	0	0	0	0	٥	0
	(a) (a) (b) (c) (c) (d) (d) (d) (d) (e) (d) (e) (e) (e) (e) (e) (e) (e) (e) (e) (e				•	•	•	•	•	0	•	•	0	0	0	0	0	0	0	0	0	0
	(G)				>		•	•	•	0	0	0	•	0	0	0		0	_	0	0	0
	(e) (c) = (c)				>	0	0	0	0	0	0	۰.	<b>5</b> (	5	m (	<b>5</b> (	ь.		0	•	0	<b>.</b>
	(9)			,	٠ د	0	0 (	۵.	<b>-</b> (	<b>o</b> (	2 :	<b>5</b>	٠,	3 (	٥ (	، د	n (	، د	~ (	7	0 1	
177 17	(u)			ļ		<b>5</b>	۰ د	ه د	<b>-</b> 1	7	<b>5</b>	· ·	- (	> 0	۰ د	7 •		- (	<b>&gt;</b> 1	٠:	<b>~</b> :	= •
100						۰ د	5 6	> 0	۰ د		<b>5</b> (	<b>-</b> (	•	> 0	> 0		- 0	> 0	-		- 0	
5 3.5	3			,						٠.	- «	> -		- «		> -	- c		۰.	- 0	> <	> <
7	ž.			٩	• •	> -	- <	> -		4 6	۰,	n <del>-</del>		٠ .	= 4	• •	• -	- <	> ~	, ,	٠:	-
5	ŗ.			-		•	> -				•	- (	• -	• ~	. –	٠.	۰,	. "	3 r	• -		
	(m)					• •	۰ د	<b>,</b>									-		.`-			
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3	:			•	,-	, -	•							•	. 0	•	0			•	. 0	• •
				Tetrachlorumethane	Trichloremethane	Dichloromethan	Chloromethane	Chloroethans	I-Chlorographe	2-Chloropronne	1-Chlorobutnana	2-Chlorobutane	1-Chloro-2-methylpropane	2-Chloro-2-methyloropine	1-Chloropentane	1-Chloro-3-methylbutane	2-Chloro-2-methylbutane	2-Chloro-3-methylbutane	2-Chlorobexane	-Chloroottene	-Chlorododecane	1-Chloroctadecane
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Exp. 6	<b>(</b> )	1120 (dichlovenettens) 1113 (chlepolom)		(179.2 ( 27C_JV odys chumida) 109.8 ( 28C_M odys chumida)		(cah) (choist) (11.0 (1.1-fetherwalnes) (1.2-teskroachme) (1.2-teskroachme) (1.1-terfekroachme) (hexatherpachme)	110.6 (cabyf dileride)	107 (pmdan)	112 (mycsec) 113.8 (bulsec) 114.8 (feebystene)	HILO Chalanco HILA (isobulanci				(isobutese)		111.4 Gachadame)	111,4 (isobdane)	
3	()	QF.11	111.46	100.50	109 44	100.61	riazo	178'01	110.49	110.49	100 50	107.44	3	19001	110.76	2111	111.27	107.30
9,	·©		_															
65	©																	
6,	(i)				70.56				69.51	69.51		70,56	25.05					2
L L	(s)	4092918	¢	0		4192918	c	0			c			-1.85836	0	e	-1.458.36	
٧	•	0.9/771	1.09773	1.157%		0.86339	TXXLLO.!	1.15796			1.13796			0.RI 549	1.04887	1,04887	1,04887	
i i	-	-	0.75	0.73		-	81.0	0.73			67.0			1	0,75	67.0	a,75	
ن	•	0.81317 (Eq. (15.111))	((5) 51) tp)	-		(Eq. (15.1.17)	ı	-			١ ا			1	-	-		
٦		1	a.13	-		-	87.0	-			-				87.0	0.75	0.75	
	E GAM!	11.91771	17TIV II	_		650981)	Q91771	-			1			D.M1549	171100	14160	17710.0	
3	r Į	17719.0	0.XGK10	a,KO359		GAUAGO	5(4781)	65KSAC19			030040			0.81549	201730	561-1810	กะว่ายร	
Atom 2	11) heldboden Dodgnakun (Tabla 13.1A)	1	5	=		ם	-	Z			=			ก	-	-	1	
, E	Įį	12,033	12.96764 (')	=		-12,96764 (7)	.14x0573	=			=			יןעשאו <u>ז.</u> ני	4.7 1.3	-1420575 (',	-143Q575	
Atuar I	Option 15.3 A)	-	2	-		-	5	-						ก	•	~	-	
3	į	17,0378	-16 37490	15.75491		.0575493 C.2	15.58ñ3	15.73.ED			-15.75.03			rineauri.	-15.59m3 C',	-15.58m3	15.45883	
20.	]] g	SSER	1.5%61	SEPY		8817	7.1633	Bart			3,435			4,795k	1891 7	TV TV	4.79Sx	
20, 1	įβ	1,790,1	1,3827	2199711		3,53(2)	211776	2,11006			1117904			T.219.17	21133	10,002	2,303,27	
20'	, (°	1,7947.1	3.11106	1111111		29127	131547	2,1186			11002			291547	291547	2.91347	2.90027	
Table 12-26, the color maps parameter or many properties and the color of the color		((C, -C! (I))	(E) - (7 (III)	ZHC,H ZHC,H (C' -C7 (III))	ZC_C,H,	(C; -C7 (Fil))	(C, - C7 (W))	HH.	Z.Y.Y.	н'з',ъ	LHC. H	7.7.7	H, Y, Y	7.0°C	H'J'.)7	H1507	, 20, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0	W.C.C.
															_			

## ALKYL BROMIDES $(C_n H_{2n+2-m} Br_m, n=1,2,3,4,5... \infty m=1,2,3... \infty)$

The branched-chain alkyl bromides,  $C_n H_{2n+2-m} Br_m$ , may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein 5 at least one H is replaced by a bromine. The C-Br bond comprises a functional group for each case of Br replacing a H of methane for the series  $H_{4-m}C-Br_m$ , m=1,2,3, with the C-Br bond of  $CBr_4$  comprising another functional group due to the limitation of the minimum energy of Br matched to that of the  $C2sp^3$  HO. In addition, the C-Br bond due to Br replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-Br functional groups comprises the hybridization of the 2s and 2p shells of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  hybridized orbital (HO) and the Br AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl bromides, the energy of bromine is less than the Coulombic energy between the electron and 20 proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the Br AO has an energy of  $E(Br) = -11.81381 \, eV$ . To meet the equipotential condition of the union of the C-Br  $H_2$ -type-ellipsoidal-MO with these orbitals, the 15 hybridization factor  $C_2$  of Eq. (15.52) for the C-Br-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO \text{ to } Br) = \frac{E(Br)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-11.81381 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.74081 \quad (15.112)$$

The valence energy of the carbon 2p is  $-11.2603 \, eV$  and that of the Br AO is  $-11.81381 \, eV$ . The energy difference is less than that of  $E_T(C-C,2sp^3)$  given by Eq. (14.151) for a single bond. Thus,  $E_T(atom-atom,msp^3.AO)$  of the alkyl C-Br-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is  $-0.92918 \, eV$  (Eq. (14.513) based on 5 the maximum single-bond-energy contribution of the  $C2sp^3$  HO.  $E_T(atom-atom,msp^3.AO)$  of the series  $CBr_mH_{4-m}$  m=1,2,3 is equivalent to those of methyl groups,  $-0.72457 \, eV$  (Eq. (14.151)). For  $CBr_4$ ,  $E_T(atom-atom,msp^3.AO)$  of the C-Br-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is  $-0.36229 \, eV$  (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of s=1,  $E_T(atom-atom,msp^3.AO)=-0.72457 \, eV$ 

The symbols of the functional groups of branched-chain alkyl bromides are given in Table 15.39. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl bromides are given in Tables 15.40, 15.41, and 15.42, respectively. The total energy of each branched-chain 15 alkyl bromide given in Table 15.43 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.42 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that was subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHBr group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CBr group (no H bonds to C) were each treated as a tert-butyl C-C.  $E_{mag}$  is subtracted for each t-butyl group. In the case of 2,3-dibromo-2-methylbutane,  $E_{mag}$  is positive since the terms due to the two bromine atoms cancel that of the t-butyl and CH groups. The bond angle parameters of branched-chain alkyl bromides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.112) are given in Table 15.44.

Table 15.39. The symbols of functional groups of branched-chain alkyl bromides.

E. diamal Graye	Group Symbol
Functional Group	Group Symbol
CBr of $CBr_m H_{4-m}$	C-Br (i)
CBr of CBr <sub>4</sub>	C-Br (ii)
CBr of $C_n H_{2n+2-m} Br_m$	$\dot{C}-Br$ (iii)
CH₃ group	$C-H$ $(CH_3)$
CH₂ group	$C-H\left(CH_{2}\right)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

0.49298 0.47279 0.49298

0,38518

0.18708 0.2933 0.29736

0.45137

0,51338 0,50570 0.51388

0,38106

0.33413

ار ق

0.33413 D.36734 0.3673H

					_,	_
C-C (f) Group	2.10725	1,45164	1.53633	1.532 (propare) 1.531 (butane)	1,52750	0.68888
C~C (e) Group	2.10725	1.45164	(,53653	1.532 (propane) 1.531 (butane)	1.52750	0.68888
C-C (d) Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0,68600
C-C (c) Group	2,10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
C-C (b) Group	2.12499	1,45744	1.54280	1.532 (propens) 1.531 (butane)	1.54616	0.68600
C – C (a) Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600
C-H Group	1.67463	1.05661	1,11827	1, 122 (isobutane)	1.29924	0.63095
C-H (CH <sub>3</sub> )	1.67122	1.05553	1.11713	1.107 (C-H propane) 1.117 (C-H butane)	1.29569	0.63159
CH (CH,) Group	1.64920	1.04856	1,10974	1,107 (C-H propane) 1,117 (C-H butane)	1,27295	0.63580
C - Br (iii) Group	2,47329	1.82719	180361	1.93 (1.1.1-tribromocthane) 1.950 (1.2-dibromocthane)	1.66889	0.73877
C - Br (ii)	2,52509	1.84622	1.953%	1.935 (Carbon tembranido)	1.72265	0,73115
Parameter C-Br (i) C-Br (ii) C-Br Group Group	2,49163	1.83395	1.94097	1,953 (mathyl bramido)	1.68667	0,73604
Parameter	0 (a,)	(°, (°	Bond Cength	Exp. Bond Length	b,c (a,)	ľ

Table 15.41. The MO to HO intercept geometrical band parameters of branched-clain alkyl branides. R.R.H." are H or alkyl groups.	etrical bond	f parameters of b	ranched-cliain a	Ikyl bromides. 1	R.R.R" are H	or alkyl groups		Er is Er (atom-atom, msp'.AO).	, 40).		1	i		
Bond	Atom	, F.	E,	17	12,	Final Total	Ţ	.1	Enter	E(CZy)	.0	6	<b>6</b> ,	q
		(eV) Bond I	(eV) Bond 2	(eV) Band 3	(eV) Bond 4	('2 <i>sp</i> '	(°)	(°)	(ev) Pinal	· (eV) Final	· (C)	©	©	(%)
$H_{L=0}(1-Br_{m}, m = 1,2,3,$ $(C_{m} - Br_{m})$	ن	41,36229	c	c	0	-151.97798	17716.0	0.K95K2	-15.18804	-14.99717	68.10	111.90	25.02	2.1680
$H_{1-a}C_{a} - br_{a}$ , $m = 1.2.3$ , $(C_{a} - Br_{a})$	Br	0.36229	6	0	0		1.15169	0.89582	-(5,fx104		68.10	06111	25.02	2.1680
(C, Hz, (C, - Br (ii))	ن	-0.18114	u	٥	0	CH967.121.	12216:0	₽90664	-15,00689	-14 81603	64.10	113.90	28.76	2213
(', lb, (C, - Br (ii))	8.	40,18114	0	·	0		1.13169	0.90664	-13.00689	· -	64,10	113.90	28.76	2213
$-H_{i}(\cdot,i',B^{r})$ $(C_{i}-B^{r})$	٠,	-0,46459	81626'0-	0	0	-153,00946	0.91771	0.N3NRS	-16.21952	.16.02866	62.67	11733	26.35	2177
-H, (', ', 'hr (C, - Br (iii))	H.	-0,46450	t.	0	0		1.15169	0.88983	-15.29034		61.69	110.81	29.93	2143
C-H (CH,)		R1020.0-	a	•	Ð	-152.54487	17710.0	0.KG35V	-15.75493	-13.36407	77.49	12201	41,48	1,238
C-H (CH <sub>2</sub> )	i	×1020.0-	*1929.0-	۰	c	-153,47406	17716.0	0.81549	-16.68412	-16.49325	CH.47	111.53	35.84	1.35
C-H (CH)	٠	40.9291K	.0.9291%	A1.9291R	O	-154.40324	17116.0	0.77247	-17,61330	-17,42244	61.10	118,90	31.37	1,4209
H,C,C,H,C'H, —	ن.	-0.9291R	0	ø	Ð	-152.54487	1,24,10,0	0.86359	-15.75493	-15.56407	63,82	116.18	30.08	1.8317
H,C,C,H,C,H,-	::	A192918	-0.92918	۰	Û	-153.47406	177160	0.81549	-16.68412	-16,49325	56.41	13.39	26.05	1.9085
$R - H_1 C_2 (H_1 C_2 - R) H H_2 - (C - C C)$	ن	81020,0-	41:92918	-0.92918	Û	-156.40324	1,711,0,0	0.77247	-17,61330	-17,42244	48.30	131.70	21.90	1.9716
$R-H_2C_a(R^a-H_3C_a)C_a(R^a-H_3C_a)CH_2-$	ئ	H16Z6.0-	-0.72457	-0.72457	-0.72457	-154,71860	0,91771	0.75889	-17.92866	47.57.51-	48.23	131.79	21.74	1.9573
(suc_C; (H; c, -R) HCH; -	ئن	X10 <u>5</u> 20.0-	-0.92918	#1020,0-	0	154,40324	0.91771	0.77247	-17.61330	-17.42244	4\$30	131.70	21.90	1.9710
$(U-U, (R-H_2C_s)U, (R-H_2C_s)CH_2 - (U-C, (e))$	ڻ	-0.7MS7	-0.72457	-0.72457	-0.72457	-154,51399	0.91771	0,76765	-17.92866	e7757.71-	\$0,04	129.96	22.66	1946
(C-C, (f)) $(C-C, (f))$	'''	-0.72457	-0.92918	-0.9291R	4	- [54, 19863	0.91771	0,78155	.17,408(?)	.17.21763	52.78	17,72	24.04	1934
(C'-C', G')	. :	-0.72457	A72457	.a.72457	-0.72457	-154,51309	0.91771	0.76763	-17.92866	פתנה.וו.	50.04	129.96	22.66	45.

Table 15.42. The energy parameter	rs (eV) of function	_	groups of branched-chain alkyl brannides.	ranides.								
Parameters C-8r	C-8r		C-Br	CH,	CH,	H-3	(a)	(S)	(e)	(g)	(e) (c) (c)	€ 0-0
	€	<b>⊕</b>	9	Oroup	Group	ф 5	drong	daes	dies	die D	dress	dan.
	-	-	-	3	2	-	_	-	-	_		1
		٥	٥	7	-	•		0	0	0	0	0
-			•	0			0	0	0	0	0	0
	0.5	0.5	. 0.5	0.75	0.75	0.75	0.5	0.5	50	0.5	0.5	0.5
	0.74081	0.74081	0.74081	-	-	-	-	1	-	J	1	. 1
4	-	_	-	-	_	-	-		-	1	1	1
	-	-		0,91771	177160	177160	0.91771	17716.0	0.91771	17712.0	17716.0	0.91771
7	0	٥	٥	0	-	-	0	0	0	1	1 1	0
6	~	7	7	_	-	_	7	2	2	2	2	3
	۰	•	٥		7	-	0	•	0	0	0	0
	20	0,5	0.5	0.73	0.75	0.75	0.5	0.5	2,0	0.5	0.5	0.5
	0.74081	0.74081	0.74081	-	-	-	-	-	-	-	-	1 .
(4)	-27.94806	-27.44996	-28.22940	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
1, (aV)	7.41885	7.36953	7.44631	38.92728	25.78002	12.87680	9.33352	9,33352	9.37273	9,33352	9,37273	9.37273
7 (eV)	\$ 60839	5,43544	5.70686	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	00\$06'9	6.90500
Z (e.Z.)	-2.80419	-2.71772	-2.85343	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E[.a no] (cV)	-14.63489	-14.63489	14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15,56407	-15,35946	-15.56407	-15.35946	-15.35946
ΔΕ, 12 (40 m) (eV)	-0.72457	-0.36229	-0.92918	0	0	0	0	0	0	0	0	٥
E. Lo m) (cV)	-13.91032	-14,27260	-13,70571	-15.56407	-13.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15,35946	-15.35946
E, (u, sm) (cV)	-31,63533	-31,63531	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
fi. (atum - atom, nisp3.AO) (cV)	-0.72457	-0.36229	-0.92918	0	0	0	1.85836	-1.85836	-1.44915	-1.85836	-1,44915	-1.44915
E. (sa) (eV)	-32,35994	-31,99766	-32,56455	-67,69450	-49.66493	-31,63537	-33.49373	-33,49373	-33.08452	-33.49373	-33,08452	-33.08452
1013 malls)	6.39733	6,27059	6.46864	24.9286	1872.42	24.1759	9,43699	9.43699	15.4846	9.43699	9,55643	9,55643
E. (eV)	4.21083	4,12741	4.25777	16.40846	15,97831	15.91299	6.211.59	621159	10.19220	6,21159	6.29021	6.29021
(eV)	-0.13137	-0.12861	-0.13293	-0.25352	-0.25017	-0.24956	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
F. Cor (0V)	0.07575	0.08332	0.07575	0.35532 (Eo. ((3.458))	0.35532 (Eo. (13.458))	0.35532 (Eq. (13.458))	0,12312 [2]	0.17978 [4]	0.09944	0.12312 [2]	0.12312	0,12312 [2]
F. (eV)	-0.09349	-0.08695	-0.09506	-0,22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
F_ (aV)	0.14803	0,14803.	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
1. ( tamp) (aV)	-32,45343	-32.08460	-32,65961	-67.92207	-49.80996	-31.70737	-35.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
F L, in my (eV)	14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489
1: (iv m) (aV)	0	. 0	0	-13,59844	-13.59844	-13.59844	0	٥	0	0	٥	٥
E (m) (c)	3.18365	2,81482	3.38983	12.49186	7.83016	3.32601	432754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 13.43. The total bond energies of branched-chain alkyl branides calculated using the functional group compositions and the energies of Table 13.42 compared to the experimental values [3]. The magnetic energy  $E_{aa}$  that is subtracted from the weighted num of the  $E_{a}[e_{aa}]$  (e?) values based on formula Name C = In (ii) C = In (iii) C + In (ivial C + In (ivial

Relative Error	0.00366 0.00323 0.00360	-0.00093 -0.00093	0.00007	0.00033	-0.00028																					
	11.196 12.919 15.712	40.160	75.05 75 75 75 75 75 75 75 75 75 75 75 75 75	100.952	198.194			,																		
	11,25929 12,87698 15,67551	40,19709	68.48143 76.67019 88 87780	100.98559	196.44719	Byp. 0	:	(methyl tramida) 113.2 (difrementations)	(https://district.org/	(dibramomethane)		110 (12-diferencellane)	1.14rihrumestuma)	109.5 (1,1-ditromocthans)	(mmm)	112 (propine) 1138 (brunna)	(terbotanc)	(heatens)				110.R (lasbutanc)		7	(technisms)	(inchatana)
i G	7000	00	000	000		. o .		11200	5		05,601	7 6	-+	- E	77 80	69 111	+	10.49	05,001	100.44	109.44	<i>1</i> 9011	110.76	11111	l m	5
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						æ. €	-	<u> </u>															T		T	†
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		000	•••	• • •	maneters from	ڻ		-	67.5		-			-	-				-			_	87.5	6.73	0.75	ľ
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Tetrabromomethane	Tribronometane Bronomethane Bronostians [-Bronomean	Bromoprap -Dibromo-	l-Bromokexane 1-Bromokaptane 1-Bromoctane	Bramodode	e bond any	# <u>1</u> 5		3 CGT/III	3.111/06	118000			191617		Sill like				╌	T	+-	1.21547	2,91547	191517	2,943.27	
f '					Table 15.44. The bond angle parameters of branched-chain alkyl bromides and	( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( )		(C, - Br (I))	CHC, Br (C, - Br (III))	н'.нг	((', - Br (ii))	ZC', 'H', (C', - Br (iii))	ZC,C, Br	(C Mr (iii))	H, H		H*5'.)7	Nethyl	5.5.77	#3.37	7.7.7		# C. H			4,C,C,

ALKYL IODIDES 
$$(C_n H_{2n+2-m} I_m, n=1,2,3,4,5... \infty m=1,2,3... \infty)$$

The branched-chain alkyl iodides,  $C_nH_{2n+2-m}I_m$ , may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein 5 at least one H is replaced by an iodine atom. The C-I bond comprises a functional group for I replacing a H of methane  $(CH_3I)$  or for I replacing a H of an alkane corresponding to the series  $C_nH_{2n+2-m}I_m$ . The C-I bond of each of  $CH_2I_2$  and  $CHI_3$  comprise separate functional groups due to the limitation of the minimum energy of I matched to that of the  $C2sp^3$  HO. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $(CH_3)_2CH$  and t-butyl  $(CH_3)_3C$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

- The solution of the C-I functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the I AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl iodides, the energy of iodine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq.
- 20 (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \ eV$  (Eq. (15.25)). The I AO has an energy of  $E(I) = -10.45126 \ eV$ . To meet the equipotential condition of the union of the C-I  $H_2$ -type-ellipsoidal-MO with

these orbitals, the hybridization factor  $C_2$  of Eq. (15.51) for the C-I-bond MO given by Eqs.

25 (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ I\right) = \frac{E(I)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-10.45126\ eV}{-14.63489\ eV}(0.91771) = 0.65537 \quad (15.113)$$

The valence energy of the carbon 2p is  $-11.2603 \, eV$  and that of the I AO is  $-10.45126 \, eV$ . The energy difference is positive. Thus, based on the maximum charge density on the  $C2sp^3$ 

HO  $E_T(atom-atom,msp^3.AO)$  of the C-I-bond MO in Eq. (15.52) due to the charge donation from the C and I atoms to the MO is -0.36229~eV (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of s=1,  $E_T(atom-atom,msp^3.AO)=-0.72457~eV$  and  $E_T(atom-atom,msp^3.AO)=0$ ) for methyl and alkyl iodides, -0.18114~eV for diiodomethane, 5 and 0 for  $CHI_3$ .

The symbols of the functional groups of branched-chain alkyl iodides are given in Table 15.45. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl iodides are given in Tables 15.46, 15.47, and 15.48, respectively. The total energy of each branched-chain alkyl iodide given in Table 15.49 was calculated as the sum over the integer multiple of each  $E_D(G_{CPRUP})$  of Table 15.48 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that was subtracted from the weighted sum of the  $E_D(G_{CRUP})$  (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHI group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CI group (no H bonds to C) were each treated as a tert-butyl C-C.  $E_{mag}$  is subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl iodides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.113) are given in Table 15.50.

20 Table 15.45. The symbols of functional groups of branched-chain alkyl iodides.

Functional Group	Group Symbol
CI of $CH_3I$ and $C_nH_{2n+2-m}I_m$	C-1 (i)
CI of $CH_2I_2$	C-I (ii)
CI of CHI <sub>3</sub>	C-I (iii)
CH₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H$ $\left(CH_{2}\right)$
СН	. <i>C – H</i>
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

							_	_		_
(i) 2-2	Group	2.10725	1.45164	1.53635	1.532	(propane)	1.531	(butane)	1.52750	888890
(e) 2-2	Group	2.10725	1,45164	1.53635	1.532	(properse)	1.531	(butane)	1.52750	0.68888
(p) 2-2	Group	2.12499	1.45744	1.54280	1.532	(bendond)	ES:1	(butane)	1.54616	0 68600
(e) 2-2	Group	2.10725	1,45164	1.53635	1,532	(brobgue)	1531	(butane)	1.52750	0.48888
(q) コーン	Отопр	2.12499	1.45744	1.54280	1.532	(brobane)	1531	(butane)	1.54516	OVEROO
C-C (a)	Oroup	2.12499	1.45744	1.54280	1,532	(propene)	1531	(butzme)	1.54616	007870
H-3	Group	1.67465	1.05661	1.11827		1.12	(isobutane)		1.29924	300590
C-H (CH.)	Orano	1.67122	1.05553	-1,11713	1.107	(C-H propane)	1.117	(C-H butane)	1,29569	031690
C-H (CH.)	Group	1.64920	1.04856	1,10974	1.107				1,27295	083690
(III) /-3	Group	2,70662	2.03222	2,15081		2.15	(carbon totraiodida)		0.787.1	50034
(II) 1-3	Group	2.68865	2.02546	2.14365		2.132	(methyl iodide)		1.76815	75534
(i) /-3	Group	2.67103	2,01881	2,13662		2.132	(methyl indide)		1,74894	0.76697
Perenter		a (a")	c' (a,)	Bond Lenyth 2e* (A)	Exp. Bond				b, c (a,)	
	(ii) $C-H(CH)$ (iii) $C-H(CH)$ (iv) $C-C$ (	(iii)	(iii) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-C (e) C-C (b) C-C (c) C-C (d) C-C (e) C-C	(iii) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) Group	(iii) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-C (ii) C-C (iii) C-C (iii) C-C (iii) C-C (iii) C-C (iiii) C-C (iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii	(iii) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-C (ii) C-C (ii) C-C (ii) C-C (ii) C-C (iii) C-C (iii) C-C (iii) C-C (iii) C-C (iiii) C-C (iiii) Chaup Graup II,67122 II,6746 II,6744 II,4744 IIII II,4744 II,4	(iii) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-C (a) C-C (b) C-C (b) C-C (c) C-C	(iii) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-C (ii) C-C (ii) C-C (ii) C-C (ii) C-C (iii) C-C (iii) C-C (iii) C-C (iii) C-C (iiii) C-C (iiii) C-C (iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii	(iii) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-C (b) C-C (c) C-C C-C (c)	(iii) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-H (CH <sub>3</sub> ) C-C (b) C-C (c) C-C C-C (c) C-C C-C (c) C-C C-C (c)

Take 16 47 The MO on 110 intercent manuscribed hand narranteers of branched-chain alkel foldides. R.R.R. as H or alkel groups.	mical fond	narameters of br	anched-chain ali	lyd iodides. R.	R. R. are H or		E, is E, atom	E. is E. (atom - atom, msp'.AO)	<u>6</u>						
Bond	Atom	(e, F,	F. (9.	[eV.]	F. (§)		[a]	J. @	Final Co.	E(C24p²)	is ©	e-©	6 O	A (9,	(a, 2, 4)
		Bond 1	2 pung	Bond 3	+ 50000	<b>1 3</b>				E I					
(H,1	Ü	-0.1x11d	a	. 0	0	-151.79683	17116.0	0.90664	-15.00689	-14,£1603	63.63	110.37	29.08	2340	031360
(CH.)	`	-0,18174		0	0		1,30(83	0.90664	-13.00689		69,63	75,011	29,03	23342	031560
(() ( - 3)	ن	-0.[8][4	-0.92918	·	ь	-152.72602	17116.0	0,85377	-15.93608	-15.7452[	63.16	116.84	2822	2.40436	0,38554
1554-	-	-0.18114	•				130(13	0.90464	-15.00689		69.63	110.37	19,01	23342	03150
(C - 1 (fl))	'n,	15060.0-	•	e e	۰	-131,70626	17116.0	B.91214	.14,91632	-14.72546	68.61	85111	12.71	2,35818	0.33272
(C, H, I)	-	-0.09057	0	•	۰		£310£7	0,91214	-14.91632		68.61	65111	24.71	2,35818	0,33772
C,H,	ن	0		·	°	-151,61509	17710.0	171160	-14.82575	-14,63489	67,56	112.44	28.32	2,31256	0.35035
C,H,	-	c		۰			1,30183	126160	-14.92575	-14,03489	67.56	112.44	1831	2,31256	0.35035
$C \rightarrow H(CH_s)$	U	-0.92918		۰	۰	-152.54487	17719.0	0.86359	-13.73493	-13.36407	77.49	16,201	81'18	1,23564	Q.18708
C-H (CH.)	ľ	-0.92918	-0.9291E	0		-153,47406	17710.0	0.81549	-16,68412	-16,49325	68.47	111.53	35,84	1,35416	0.29933
C-H (CH)	Ü	40.92918	-0.92918	×16250-	0	-154,40324	0.91771	0,77247	-17,61330	-17,42344	61.10	118.90	31.37	1.42918	0.37326
H,C,C,H,CH2-	ن	-0.92918	e	o		-152.54417	17716.0	0.16359	-15,75493	-13.56407	63.82	116.18	30,0\$	1.83879	0.38106
HCC, HCHz-	ئ	-0,9291X	*16ZG-0-	o	٥	-153,47406	17716.0	0.81549	-16,61412	-16,49325	56.41	13.59	26.06	1.90190	0.63117
R-H2C.(H3C,-R)HCH1-	ť	-0.9291#	X16Z6'0-	-0.92912	0	-154,40324	17710	14277.0	-17,61330	-(7,42244	48.30	07.161	21.90	1,971@	0.51388
$R - Hf_{-}(R - Hf_{-})C_{+}(R - Hf_{-})C_{+}$	ť	-0.9291R	-0.72457	-0.72457	-0.72457	-154,71860	17716.0	0.75889	-17,92866	417,717-	404.21	Ø7.181	21.74	1.95734	0.50570
100°C, (H,C, -R)HCH <sub>3</sub> -	ئ	40,9291R	#10ZG-0-	-0.92918	0	-154.40024	17716.0	0.77247	-17,61330	-17,42244	48.30	02:111	21.90	1,97162	0.51388
$(R - R_3C_s)C_s(R - H_2C_s)C_s$	ئ	4,72457	-0.72457	477457	.0.72457	-154,51399	17716.0	0.78763	-17,92866	-17.73779	50.04	32,627.1	22.66	1,94462	0.49298
(c'-C' (f))	ئ	-0.72457	-0.52918	-Q.9291K	9	-154,19163	17716.0	0.78155	-17.40RGD	-17.21783	52.78	22.23	24.04	1,92443	0.47279
kuC_(R'-H,C_)C,(R'-H,C_)CH_2-	ئ	-0.72457	-0,72457	4,72457	PALT.O.	-15451389	17116.0	0.76765	-17,92866	-17.73779	\$0.04	129.96	22.66	1,94462	0.49258

Dommeran	]	13	7	7	7.	- H-D	(E)	(A)	(S)	(e)	ر-ر د-رو	3,-,
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	-	-		0.91771	0.91771	17110	0.91771	177160	0.91771	0.91771	17710.0	17716.0
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2	0.65537	0,65537	0.65537	-	_	-	-		-	1	1	1
V (aV)	-26.59109	-26.34902	-26,10696	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V (eV)	6.73951	6.71739	6.69505	38.92728	25.78002	12.87680	9,33352	9.33322	9.37273	9.33352	9.37275	9.37275
T (eV)	4.97768	4.90005	4.82280	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6,90500	6.90500
V (eV)	-2.48884	-2.45002	-2.41140	-16,26957	-10,53337	-5.24291	-3,38732	-3,38732	-3.45250	-3,38732	-3.45250	-3.45250
E(w no) (cV)	-14,63489	-14,63489	-14,63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15,36407	-15.35946	-15.35946
DE ann (w m) (aV)	-0.36229	-0.18114	•		0	0	0	0	0	0	0	٥
E. (10 10) (eV)	-14.29907	-14,45375	-14,63489	-15,56407	-15.56407	-14,65489	-15.56407	-15,56407	-15.35946	-15.56407	-15.35946	-15.35946
E. (u, sa) (eV)	-31.63534	-31,63535	-31,63540	-67,69451	-49.66493	-31,63533	-31,63537	-31.63537	-31,63535	-31.63537	-31,63535	-31.63535
E. (aton - atom, msp' AO) (eV)	-0.36229	-0.18114	°	٥	٥	•	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E. (va) (eV)	-31.99766	-31.81651	-31,63537	-67,69450	-49.66493	-31.63537	-33,49373	-33,49373	-33.08452	-33,49373	-33.08452	-33.08452
w (10th rod/s)	10.2318	5.36799	9,90080	24.9286	24.275!	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
E. (eV)	6.73472	3.5331	6.51688	16.40846	15,97831	15.91299	6,21159	621159	10.19220	6.21159	6.29021	6.29021
E (aV)	-0.16428	-0,11832	-0.15977	-0.25352	-0,25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Exa (eV)	0.06608	0.06608	0.06608	0.35532 (Eq. (13.458))	0,35532 (Eq. (13,458))	0.35532 (Eq. (13.458))	0.12312 (2)	0.17978	0.09944 [5]	0.12312 (2)	0.12312 [2]	0.12312 [2]
E (al)	-0.13124	-0.08527	-0.12673	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_ (eV)	0,14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. (Dun) (aV)	-32.12889	-31,90179	-31.76210	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33,24376	-33.59732	-33.18712	-33.18712
E (1, 10,110) (aV)	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
E (a) (a) (aV)	. 0	0	0	-13,59844	-13,59844	-13.59844	0	0	0	0	0	0
E. tona) (0V)	2,71108	2,63201	2.34429	12,49186	7,83016	3.32601	4,32754	4,29921	3.97398	4.17951	3.62128	3.91734

Table 15.49. The total bond energies of branched-chain alkyl loddies calculated using the functional group composition and the energies of Table 15.48 compared to the experimental values [2]. The magnetic energy  $E_{-ac}$  that is subtracted from the weighted sum of the  $E_0[c_{-ac}]$  (eV) values on composition is given by (15.58).

Relative Ecror	0.00444	2000	-0.00263	990000	900000	0,0000	-0.00119
Experimental Total Bond Energy (cV)	10,405	12,921	15.163	27,343	39,516	FT 9'65	51,899
Calculated Total Bond Energy (eV)	10.33888	12,94614	15,20294	13005.15	39,51834	39,61923	\$1,96057
E E	•	7		٥	٥	0	-
ر( <u>)</u> د–د		0	0	۰	0	0	•
(e) C-C (e)	•	•	•	۰	٥	0	٥
C-C (d)			0	٥		0	С
(e) C-C	c			•		6	3
(4) 2-2			•	•			0
(a) 2-2	•	, .		. –		•	0
(E) #3	-						c
() H.)							- 0
CH,	-	= -			۰,	1 2	
<i>CH</i> ;		•	• -			- •	<b>1</b> m
(III)		۰.	3 5		<b>3</b> 6	2 9	
(11)			7 6	5 6		2 0	- 6
C-1 (i)		,	٠.				
Name Name		Thiodomcibess	Ottodonocthane	Codornellano	Lodocihane	-lodoptopen	2-lodo-2-meth-formatic
Formula		<b>3</b>	Š	Ē	E C	£5	

Esp. 0	C			111.2 (medty1 bodide)			107 (propane)	112 (propane) 113.8 (butane) 110.8 (sobutane)	(111.0 (britano) 111.4 (teobatane)				ROII (Sobutare)		111.4 (isobetare)	(111.4 (isobutane)	
3,	•€	112.10	112.39	05.001	109.44	111.16	10%	110,49	110.49	109.50	100.44	109,44	110.67	110.76	111.27	111.27	02,701
o,	<u> </u>																
9	<u> </u>																L
	<u> </u>				70.5E			15.00	1500		70.56	70.36					72.50
E,	(§)	-0.3622B	0			8229E0-	۰			٥			-1.85836	0	0	-1,55836	
5		1	00000'1	1,15796		0.87495	1.15796			1,15796			0,81549	1.04887	1.04887	1.04187	
J		-	0.75	6,75		-	87.9			67.5			1	62'0	6.73	6.75	
Ů		0.65537 " (Eq. (15.113))	0,76215 (Eq.(15.63))			0,63337 (Eq. (15.113))	1			1			1	1	1	1	
ť		1	D.73	-		1	-						1	67.0	67.0	0,75	
	Ather 2	-	17716.0	-		0 87495	-			-			G+\$1#'0	12416'0	11416.0	11718.0	
ζ,	Atms 1	-	17710.0	0.NG359	:	0,87405	0,86349			0.86359			0,81549	0.87493	0.R7495	0,17495	
About Remain Remain C. C. C. C. C. C. E.	Designation (Toble 15.3.A)	-	-	æ		-	æ			æ			<b>8</b> 2	-	-	-	
F.	V Para 3	-10,45126	1045126	I		-10,45126	=			Ŧ			2148531.	-14.82575 C.	-14.82575 C,	-14,82575	
Atom 1	Calgnation	-	_	~		~	-			,			ກ	ű	~	5	
1,	Alore I	-10,45126	-14.82575	-15,73493		-15.55033 (°,	-15.75493			-15.75493			-16.68412 C.	-15.55033 . C.	-15.53033 (' <sub>k</sub>	.15.55033	
, Z	Always ( a <sub>b</sub> )	6,7205	3,2203	3,4253		5.7039	3,4252			3.4232			4,7958	4,1633	4, 1633	4,795x	
2c.	<u>j</u> §	4 03092	4.03763	2.03711		4.03763	211106			2.09711			2.91547	211333	1.007.1	12500.5	
.77	18	4.03092	211106	209711		2.91547	2,11106			2.09711			291547	2.91547	2,91547	2.90327	
Absent Angle 2c' 2c' 2c' I'man		(U, -1 (III)	(C, -1 (0)	ZHC,H ZHC,H (C,-1 (0)	(C, -1 (i))	(c, -1 (i)) 20,77	Heftstere ZHC: H	ית.'נ"ני	н".5".77	H".H7	ע."נ"נ.	H",","	ייינ"נ". קנ"נ"נ"	#°C,"H T.°C,"H	".)™! """."H	#"C"C,	0.00

## ALKENYL HALIDES $(C_n H_{2n-m} X_m, n=3,4,5... \infty m=1,2,3... \infty)$

The branched-chain alkenyl halides,  $C_n H_{2n+2-m} X_m$  with X = F, Cl, Br, I, may comprise alkyl and alkenyl functional groups wherein at least one H is replaced by a halogen atom. In the case that a halogen atom replaces an alkyl H, the C-X bond comprises the alkyl-halogen 5 functional groups given in their respective sections. The alkenyl halogen C-X bond comprises a separate functional group for each case of X bonding to the C = C-bond functional group given in the Alkenes section. In addition the CH group of the moiety XCH = C comprises a functional group unique to alkenyl halides. The straight and branched-chain alkenes,  $C_n H_{2n}$ , comprise at least one carbon-carbon double bond comprising a functional group 10 that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. The three distinct functional groups given in the Alkenes section are C vinyl single bond to -C(C) = C, C vinyl single bond to -C(H) = C, and C vinyl single bond to  $-C(C) = CH_2$ . In addition,  $CH_2$  of the  $-C = CH_2$  moiety is also an alkene functional group solved in the 15 Alkenes section.

Consider the case where X=Cl substitutes for a carbon single bond or a hydrogen atom. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, two distinct C-Cl functional groups can be identified: Cl vinyl single bond to Cl and Cl vinyl single bond to Cl and Cl vinyl single bond to Cl arbide Cl section except that Cl Cl and Cl vinyl single bond to the Cl and Cl vinyl single bond to the Cl and Cl section except that Cl Cl and Cl vinyl single bond to the Cl and Cl bonds.

The alkyl portion of the alkenyl halide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) 25 functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkene halides are equivalent to those in branched-chain alkanes.

 $E_T$  (atom – atom, msp<sup>3</sup>.AO) of the C = C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene,  $-2.26759 \, eV$ , given by Eq. (14.247).  $E_T$  (atom – atom, msp<sup>3</sup>.AO) of each C - C-bond MO in Eq. (15.52) is  $-1.85836 \, eV$  or  $-1.44915 \, eV$  based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 \, eV$  (Eq. (14.513), or methyl,  $-0.72457 \, eV$  (Eq. (14.151)), groups, respectively.

The solution of each C-X functional group comprises the hybridization of the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. The alkenyl C-X-bond functional groups comprise single bonds and are equivalent to those of the corresponding alkyl halides except that the halogen AO and the C-X-bond MO are each energy matched to the alkene  $C2sp^3$  HO. In alkenyl halides with X = Cl, Br, or I, the energy of the halogen atom is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. For example, the hybridization factor  $C_2$  of Eq. (15.52) for the alkenyl C-Cl-bond MO given by Eq. (15.111) is  $C_2(C2sp^3HO \text{ to } Cl) = 0.81317$ .

 $E_T(atom-atom, msp^3.AO)$  of the alkenyl C-Cl-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is -0.72457~eV for the Cl vinyl single 20 bond to -C(H)=C C-Cl group and -0.92918~eV for the Cl vinyl single bond to -C(C)=C C-Cl group. It is based on the energy match between the Cl atom and the  $C2sp^3$  HO of an unsubstituted vinyl group and a substituted vinyl group given by Eqs. (14.151) and (14.513), respectively.

The symbols of the functional groups of branched-chain alkenyl chlorides are given in Table 15.51. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkenyl chlorides are given in Tables 15.52, 15.53, and 15.54, respectively. The total energy of each branched-chain alkenyl chloride given in Table 15.55 was calculated as the sum over the integer multiple of each  $E_D$  (Group) of Table 15.54 corresponding to functional-group composition of the molecule.

The bond angle parameters of branched-chain alkenyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.56.

Table 15.51. The symbols of functional groups of branched-chain alkenyl chlorides.

Table 13.31. The symbols of full chomat grou	ps of of ancheu-chain ancery's chieffaces.
Functional Group	Group Symbol
Cl vinyl single bond to -C(H)=C	C-Cl (i)
Cl vinyl single bond to -C(C)=C	C-Cl (ii)
CC double bond	C = C
C vinyl single bond to -C(C)=C	C-C (i)
C vinyl single bond to -C(H)=C	C-C (ii)
C vinyl single bond to -C(C))=CH <sub>2</sub>	<i>C – C</i> (iii)
CH (alkenyl halide)	C-H (i)
CH <sub>2</sub> alkenyl group	$C-H\left(CH_{2}\right)$ (i)
CH <sub>3</sub> group	$C-H$ $(CH_3)$
CH₂ alkyl group	$C-H\left(CH_{2}\right)$ (ii)
CH (alkyl)	C – H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Parameter	The geometrical by	밁	C=C	n alkenvl chloride	lorides and experimental values [1]	C-C (iii)	C-H (CH1)	C-H (I)	C-H (CH,)   C	C-H (CH,)	C-H (ii)	C-C (a)	(a) 2-2	(e)	(g) (G)	(e) U-U	€.
	garage Garage	(E) Quant	Group	dranb	Group	dra orb	(i) Group	diana	Group	(ii) Group	diano	diagra	dram	dran	composition of the composition o	9	dron
0 (0.)	2.15818	2,19358	1.47228	2.04740	2.04740	2.04740	1,64010	1,60061	1.64920	1.67122	1.67465	2.12499	2,12499	2,10725	2.12499	2,10725	725
c. (a,	1,62912	1,64243	1.26661	1,43087	1,43017	1.43087	1.04566	1.03299	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	3
Bond Length	1.72419	1.73827	1.34052	1.51437	1.51437	1.51437	1.10668	1,09327	1.10974	1.11713	1,11827	1.54280	1.54280	1,53635	1,54280	1.53635	×
Exp. Bond Length	1.730 (vinyl chloride) 1.73 (1.1- dehiuncikylens	(vary chloride) (1.73 (1.1- dechlurochylcze)	1342 (2- methylpsysne) 1,346 (3-hine) 1,349		1.508 (2-fruicma)	1,508 C) enertyaltiflem	1.10 C. mediv/inspana) 1.108 (avg.) (1,3-hutalisme)	1.09 (vite) chlorida)	1.107 (C-H propage (1.17 (1.17 butane)	1.107 (C-H propane) 1.117 (C-H butane)	27.1 (singhopsis)	1532 (propane) 1531 (prane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1,532 (propane) 1,531 (butane)	1.532 (propane) 1.531 (butane)	12 (St. 12 (St
b, o (a_)	1.41552	1.45403	0.75055	1.46439	1.46439	1.46439	1.26354	1,72265	1,27295	1.29369	1.29924	1,54616	1.54616	1.52750	1.54616	1.52750	8
	0.75486	0.74874	0.86030	0.69887	0.69887	0.69887	0.63756	0.64537	0.63580	0.63159	0,63095	0.68600	0.68600	0.68888	0.68600	0.68888	8

Table 15.53. The MO to HO intercept geometrical bond parameters of branched-chain alkenyl chlorides.	etrical bon	d parameters of l	branched-chain a	Ikenyl chlorides	H, R', R" are	H or alkyl groups.	5	is E <sub>r</sub> (alam – alam, mgr'.AO)	141'AO).						
. Bond	Atom	(eV) Bond 1	(eV) Bond 3	ہم (دV) Bond 3	ڊئ (eV) Bond 4	Final Total Energy ('24p <sup>‡</sup> (eV)	]()	(e)	f,((-2,p²) (6V) Final	E(C'249*) (eV) Final	.e (e)	, (C)	(e)	(°o) q'	(a, d,
$C_{\bullet} = C_{\bullet}(CI) - H_{\bullet}(CH)(I)$	ن:	-1.34946	תשנום	c	e	-153 47406	Q91771	0.81549	-16.68412	-16,49325	76.99	103.01	40.53	1,21653	0.18354
$-C_b = C_c / H / C /$	ن	97.I.I-	האנה	0	C	90tru*851-	17719,0	6451KD	Z118991-	-16.40325	79 43	100,57	74.45	1,77672	0.14360
-C' = C'(H)CI	C	r21st2r	С	0	£		1.05158	0,87495	15.55033		\$5.28	78.64	38.03	1.69995	0.07085
-(', -(')(')') ((', -(') (ii))	J.	1.13379	-0.46439	#16260°	C	-154 14326	17716.0	0.78475	58856.71-	-17.15245	73 57	107.63	JO.RB	1,603.53	0.24010
-ر* = (;'(ت)(ر) ((ر* – در (۱۱))	מ	がらまるより	8	0	0		85150,1	0.88943	-15.19034		81.62	96,38	37.46	1.74125	288CD 0
C,(H)C, = C,H,C,	΄υ	-1.13380	-0.9291K	ο.	0	-153 67867	0.91771	0 80561	-16.88873	-16 69786	127.61	52.39	58.24	0.77492	0.49168
$C_{\nu}(H)C_{\nu}=C_{\nu}H_{\nu}$	C,	-1.t31k0	o	o	c	-152,74949	0,91771	0.R5252	-15.93955	-15.76868	129.84	\$0.16	60.70	0.72040	0.54620
C(C)C = CH:C	Ů	-1.1380	-0,72457	-0,73457	0	-154.19863	17716.0	0.7K1SS	-17.40869	17,21783	126.37	1915	56.95	0.80289	0.46371
RC,H; −C,(C) = C (C − C (1)	.°	-1.13380	-0,72457	-0.73457	0	-134.19863	17716.0	0.78155	-17,40869	נמנובלו.	82 (V)	11811	67.72	1,61127	0.38039
$R(C, H_1 - C, (C)) = C$ (C - C, (0)) $R(C, H_2 - C, (C) = CH_2$ (C - C, (0))	G,	ብንዚና?	40,92918	С	ū	\$160Z (\$1-	0,91771	0.82562	16,4795)	19887 91-	67.40	112.60	31.16	1.74831	23174
$RC_{i}H_{i}-C_{i}(H)=C$ $(C-C_{i}(H))$	C.	-1.13390	*1626.0-	c	0	-133.67866	17716.0	0.80561	-16 RRICTS	.16.69736	54.57	115.43	23.79	1.77684	034596
$R_i^{C_i}H_3 - C_s(H) = C$ $(C - C_s(H))$	ς.	-0.92918	A1929.0-	0	v	-153.47.05	17718.0	0.K1549	-16 (941)	.16.49333	66.59	164.01	30.58	1.76270	633183
$C = H \left( CH_1 \right) (t)$	C	-1.13380	c	U	O	-152.74049	17716.0	0.85252	-15,95955	-15.76868	77.15	102.85	f.ts	igg.	0.18965
$C-H(CH_1)$	·	-0.92918	5	Е	0	-152.54487	0.91771	0.166359	-15.75423	13.56407	77.49	102.51	41.48	1,23564	0.18708
$C-H\left(CH_{3}\right)$ (ii)	ن	A1929.0-	×1026.0-	c	ŋ	-153.47405	0.91771	0.Rt 549	-16.6K412	-16.49325	CB 47	द्धाः।	35.64	LISARG	0.29933
C-H (CH) (ii)	Ü	NICEGU-	HIOZOGO-	816260-	0	-154,40334	0.91771	0.77247	-17,61330	-17 42244	61.10	118.90	11.37	1,42989	971778
H,C,C,H,CH; (C,C (a))	υ,	-1.92918	a	u	0	-152.54487	0.91771	0.86359	-13.75493	-15.56407	DX E9	116.18	30.08	1.63879	0.38106
$H_1(',C,H_2CH_3-(',C,-(',G)))$	C.	-0,9291R	×10£6.0∼	•	c	-153 47-106	0.91771	0,81549	16.68413	-16.49325	56.41	13.59	26.06	1.90850	0.45117
$R - H_1C_{,C_0}(H_1C_{,c} - K)H(H_1 - (C - C_1O))$	ı,	-0.5291K	#16 <u>5</u> 0.0-	\$16Z6'0-	ą	-154.47024	ונעופט	amm.	-17,61330	17,47244	0£ 83	B.181	31.90	1.97162	0.51388
$R - H_2C_3(R - H_2C_3)C_4(R^2 - H_3C_4)C'H_1 - (C' - C' (c))$	ن	-0.9291R	72127.0-	0.7357	-0.73457	-154.71850	121171	0.73889	-17.92866	917.57.51-	48.2)	67.181	21.74	1,26734	0.50570
$Ixm(\cdot,C,\{H,C,-H\}MCH,-\{C,-C,\{d\}\}\}$	ئ	-0.3291я	*!( <u>07</u> 0,0-	402218	0	-154,40324	0.91771	0.77247	0.(10.71-	HZTY'LI-	0,58	131.70	21.90	1.97162	0.51388
$RHC_{(H-H_1C_3)C_3}(H-H_1C_3)CH_1 - (C-C_1C_3)$	ڻ	-0 72457	72457.0-	4,7357	0.72457	154.51399	17716.0	0,76765	-17.522866	977.571-	र्वेड	129.96	22.00	Z9#167	26237
rent_c', (H, C, - R') H(H, - (C - C' (D)	ئ	12121	40251R	41920.0-	ė	-154,19843	17716.0	0.78155	-17.4QR69	-17.21783	51.78	27(1)	24.04	(,924)	047279
$iso(",(R'-H_1C_1)(",(R"-H_2C_1)CH_1-$	من	721.57	เรศเช	15rtt 19-	13157	44515751-	17716.0	0,76765	-17,92866	97757.51.	<b>3</b>	129.20	22.00	1.94402	0.49298

Table 15.54. The energy parameters (eV) of functional	n leV) of fund	thoma groups	of branched-ct	ain alkenyl ch	londes.								-				ر-رو
Parameters	ρ <u>()</u>	o-0 ⊚	(ii) Gram Gram Gram	() -(;	<u>e</u> .	('-('ii) Grees	C.H. C	Group Group	*, g	(E) (E)	C-H (ii)	Garage Grand	(9) U-U	(9) U-U	C. C	Group Group	Gracip
	Group	Orono	3	,	t		1	1		+-	-	-	-	-	-	-	-
=	-	1	1	-	-	-	7	-	1	•	1	1	1		,		
11	0	0	•		0	0	-	٥	7	-	•	-	-	-	,	,	٠
	0	-	•	•	0	0	•	٥	•	•	-	٠	•	•	-	-	٠
	2	S	3	20	S	S	0.75	0.75	0.75	0.75	0.75	0.5	20	0.5	2	20	2
	0.81317	0.81317	17710	-	-	-	-	-	-	-	1	ı	-	-	-	-	-
		-	-	-	-	-	-	-	-	-	-	1	-	_	_	-	-
		-	0.01771	0.91771	0.01771	17710	17710	0.91771	17716.0	0.91771	177190	17716.0	17716.0	0,91771	17719.0	17716.0	0,91771
	- -			-		-	-	-	-	-	-	•	٥	0	-	-	٥
	,	,		-	7	7	-	-	-	-	-	7	7	2	2	7	7
	٠		6	-	0	•	~	-	-	7	-	•	0	0	0	•	٥
-	,	,   ;	, , ,	ş	5	20	0.75	27.5	0.75	0.75	0.75	20	0.5	0.5	0.5	0.5	20
	215194	001313	12100	-	-	-	-	-	-	-	-	-	-	-	1	-	-
200	.17.8771	-72 14474	١,	-30.19634	-30.19634	-30,19634	-72,03287	-37,10024	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29,10112	-28.79214	-29.10112	-29.10112
(4.0)	0.25160	B 7230d		0 \$0874	9 50874	9.50874	16.02344	13.17125	38.92728	25.78002	12.87680	9,33352	933352	9.37273	9.33352	9.37273	6,37273
7. 1.0.	24148	733700	34 K70K2	737432	737432	7,37432	21.95990	11.58941	32.53914	21.06675	10.48582	6.77464	6,17464	6.90500	6.77464	6.90500	6,90500
(100)	3 80844	-3.66350	17,33531	-3 68716	-3.68716	-3.68716	-10,97995	-5.79470	-16,26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	3.45250
Et a maj (m)	-14 63489	14 61480		-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-15,56407	-15.56407	-14.63489	-15,56407	-15.56407	-15,35946	-15.56407	.15.35946	-1535946
A. Le mi (eV)	3,71674	-3.19677		۰	٥		0	-1.13379	°	0	0	0	. 0	0	c	0	٥
( ) ( ) ( ) ( ) ( )	-1001815	10 07 1 10	۰	-14.63489	-14.63489	-14.63489	-14,63489	-13,50110	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.55407	-15.35946	-15.35946
C (1.1.1) (40.7)	5	1163541	57075 83-	31.6334	-31,63534	-31.63534	49.66437	-31,63539	-67,69451	49.66493	-31.63533	7£253.1E-	-31,63537	-31.63535	-31.63537	-31.63535	-31,63535
E ( alone - about mine 40) (of)	-1 44015	0.92918	.2 26759	-1.04915	-1.85836	-1.44915	0	٥	٥	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
( (m) (n))	.33 08452	.12 56455	.65.53833	-33.08452	-33,49373	-33 08452	49.66493	-31,63537	-67,69450	49.66493	-31,63537	-33.49373	-33.49373	-33,08452	-33.49373	-33.08452	-33.08452
(10), cm(10)	21474	9.11389	43.0680	9,07851	16,4962	9.97851	15.2077	26.4826	24.9286	24.2751	24.1759	66926.6	9.43699	15.4846	9,43699	9.55643	9.55643
7	\$ 47764	5,34070	28.34813	6.56803	10,65807	6.55803	16.59214	17,43132	16.40846	15.97831	15.91299	621159	6,21159	10.19220	6,21159	6.29021	6.2902.1
(6)	-0.15312	-0.14888	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	-0.26130	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Rosa (al')	0,08059	0.08059	0.17897	0,15895	0.09931	0.09931	0.35532 Eq.	0.3532 Eq.	0.3532 Eq.	0,35532 Eq.	0.35532 Eq.	0.12312 [2]	0.17978	0.09944	0.12312	0.12312 [2]	0.12312 [2]
E 10P)	-0.11282	-0.10839	-0.25568	-0.08827	0.16869	-0.11809	72770.0	-0.08364	-0.227S7	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0,10359	-0.10260	-0.10260
( (el/)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
F. In (eV)	33 19734	-32,67314	-66,04969	-33,17279	-33.66242	-33.20260	49.81948	-31,7(901	-67.92207	-49.80996	11.70737	.33,59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E 1. 10 tm) (cF)	-14.63489	-14.63489	-14,63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489
E 14.00 may (cf.)	۰	0	-	0	٥	0	-13.59844	-13.59844	-13,59844	-13.59844	-13,59844	٥	۰	٥	٥	٥	•
E to-1 (el)	1,77953	3.40336	7,51014	3.75498	4,39264	3,78480	7.83968	3,33765	12,49186	7.83016	3,32601	4.32754	429921	3,97398	4,17951	3.62128	3.91734
, and the second ties															•		

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	e C		124 (rtegi chloride)	(Vital chloride) 1218 (1.1-dichloroathrismo)	123.8 (1,1-Schloroshykms) 123.3 (ringl chlaride)		i	13.4.1 (1.3.54exations Oncode) (1.3.54exations Carbbo Carb		118,5 (2-nethy/prepene)	121 (2-medyfpropene)	107 (propane)	111 (purject) 113 8 (purject) 110 it	(hutano) (hutano) 111.4 (hohutano)				IIas (izchutene)		111.4 (sobume)	111.4 (sobutane)	
	3 C	169	21.53	121.53	123.19	118.36	113.84	9771	118.19	116.31	121.85	10844	110.49	110.49	109.50	10:7*	102.44	110.67	110,76	111,37	11,27	107.50
	e, ©								123.46													
	e. 🖭		11694	116.94					18.36		16.51											
	ø, ©							: 	L				15.69	15.69		70.56	26.07					8,2
	(eV)	۰			-0.92918	e .	-1.89836-	92929		c		0	,		Ç			-1,85836	¢.		-1.85836	
	<b>V</b>	1.00775			ОНСТЯВ	1.07647	081340	ŞŞUZO		DOET! 1		1,15796			1.157%			0.81549	1.04887	1.04887	1.04887	
۱	,	0.75			-	0.75	_	-		67.9		0.75			67.5			-	0.73	a.73	67.5	Γ
	ָ֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖֖	0.95319 (724 (15.65))			0.81317 (15.113)	-	-	-	Ī	-		-			-			-	-	-	-	
	ບ	0.75			_	6.75	-	-		-		-			-			1	a.75	0.75	0.75	
	C, Mem 3	0.91771			U, NG 359	מישנדונו	กรเรษ	0751810 0.001540		-		-			-			6151970	0.91771	0.91771	0.9177.1	ŀ
	ره <mark>ال</mark> ا	00509.0			0.163.50	0 15252	0.81549	0,81561		252500		0.86359			0.86350			0.81540	0.87495	saresn	0.87495	
man fri man	Mons 2 Hybradication Desgration (Table 15.3.A)	5			5	1	a	7		=		=			=			ĸ	-	-	-	
Aprillaria	Erana.	-1236764 C'1			-12.967GH CJ	-14.82573	-اقرهبارا ر	-1649-111 C,		=		-			Ξ			, IG,68413 C,	-14.83575 C.	-14.R2573 C,	-14.X2575	
	Attent I Hybridization Designation (Table 15.3.A)	2				*	Ą			٠		-			-			'n	•	*	5	
Pullanti attenti	Abru 1	-tk_17450			-45.75ems	-18,95954 C,	-14,6411	-16 seb073		-15.95935		13.75.03			-15.75493			-Ingestit	.15.55#33 C.	-(5.33933 (°,	.13.55033	
	22° (a)	4.50(1)			S toward	4 JMS	#50£7	47579		347%		3,4253			3.4252	T		4.7958	11917	4.1633	4.79.58	
מבוניו אי	2¢, (a,)	2382.0			12565	206175	236175	2.16.175		104578		211106			117701			2.91347	21123	117801	2,90,127	
and offer	2c' 8 ad 1 (a,)	TWSW			2,53321	2.1133	216/73	150331	T	204578		211106			2 09711			291547	131547	1.91547	1,9037	T
I MIN E 12.50. THE DOUBLE AND THE DESCRIPTION OF THE PROPERTY OF THE PARTY OF THE P	Abores of Angle	(C, -C' (I)	(C, -C') (J)	(C, -(7)	((c' - (x) (0))	('.'(H)C'='.')	('.'(.')(.'=(.') ''(.''(.''(.'	('5'5='5) '5'5'37	J. JHZ	(H,C,=C,C)	(H'C'=C'C')	H. H.	מניני	H'5.77	Malaji ZHC H	20.07	A. C.H	'5'5'5' '7'5'5'	47,C,H 1= C,	#.C.H	α, (, (, , , , , , , , , , , , , , , , ,	ZC.C.C.

ALCOHOLS 
$$(C_n H_{2n+2} O_m, n = 1, 2, 3, 4, 5...\infty)$$

The alkyl alcohols,  $C_n H_{2n+2} O_m$ , comprise an OH functional group and two types of C-O functional groups, one for methyl alcohol and the other for general alkyl alcohols. The alkyl portion of the alkyl alcohol may comprise at least two terminal methyl groups  $(CH_3)$  at 5 each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the 10 isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alcohols are equivalent to those in branched-chain alkanes.

The *OH* functional group was solved in the Hydroxyl Radical (*OH*) section. Each C-O group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$ . 15 shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl alcohols, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the O AO has an energy of  $E(O) = -13.61806 \, eV$ . To meet the equipotential condition of the union of the C-O  $H_2$ -20 type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the

$$c_2\left(C2sp^3HO\ to\ O\right) = \frac{\dot{E}(O)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-13.61806\ eV}{-14.63489\ eV}(0.91771) = 0.85395 \quad (15.114)$$

C - O-bond MO given by Eqs. (15.68) and (15.70) is

 $E_T(atom-atom,msp^3.AO)$  of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is  $-1.65376\,eV$  for the  $CH_3-OH$  C-O group. It is based on the energy match between the OH group and the  $C2sp^3$  HO of a methyl group and is given by the linear combination of  $-0.92918\,eV$  (Eq. (14.513)) and  $-0.72457\,eV$  (Eq. (14.151)), respectively. For the alkyl C-O group,  $E_T(atom-atom,msp^3.AO)$  is  $-1.85836\,eV$ . It is based on the energy match between the O AO and the  $C2sp^3$  HO of a methylene group where both energy contributions are given by Eq. (14.513).

The symbols of the functional groups of branched-chain alkyl alcohols are given in Table 15.57. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl alcohols are given in Tables 15.58, 15.59, and 15.60, respectively. The total energy of each alkyl alcohol given in Table 15.61 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.60 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl alcohols determined using Eqs. (15.79-15.108) are given in Table 15.62.

ance 13.31. The symbols of functional groups of alkyl alcohols.	Group Symbol	НО	(£) O-U	C-0 (ii)	$C \sim H\left(CH_{j}\right)$	$C-H(CH_1)$	(. – H	((; (a)	C-C(b)	(a) U-U	C-C (d)	(;=(,(e)	(J)
, avic 13.17. Inc symbols of functi	Functional Group	ОН дточр	CHOHCO	Alkyi C-O	CH, group	CH <sub>2</sub> group	₹	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (tra t-C)	CC (t to iso-C)

Grand Grand	2.10725	1.45164	1.53635	(propane)	1.52750	
C-C (e)	2.10725	145164	1.53635	1,532 (propane) 1,531	1.52750	
C-C (d) Group	2.12499	1,45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	
C - C (e) Group	2.10725	1.45164	1.53635	1.532 (propane) 1.531 (buttane)	1.52750	
C-C (b) Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (futane)	1.54616	
C-C (a) Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (Putane)	1.54616	
Group	1.67465	1.05661	1.11827	1.122 (isobutane)	1.29924	
$C-H\left(CH_{1}\right)$	1.67122	1.05553	1.11713	1.107 (C-H propane) 1.117 (C-H butane)	1.29569	
$C-H\left(CH_{3}\right)$	1.64920	1.04856	1.10974	1.107 (C-H propane) 1.117 (C-H butane)	1.27295	
C-O (ii) Group	1,78255	1,33512	1.41303	(.431 (ethanol)	1.18107	20000
drouD C-0 (!)	1.79473	1,33968	1,41785	1,4246 (methanol)	1.19429	0 94646
dnau9	1,26430	0.91808	0.971651	0.971 (ethanol) 0.9451 (methanol)	0.86925	217616
Parameter	u (u <sub>0</sub> )	(°, (°,)	Band Length 2c' (A)	Exp. Bond Length (A)	h,c (a <sub>0</sub> )	

Table 15.59. The MO to HO intercept geometrical bond parameters of alkyl a	etrical bon	d parameters of a	ılkyi alconols. 🖊	8, R', R" are H c	slookols. R,R',R" are H or alkyl groups. $E_r$ is $E_r(ann-ann,msp^2,AO)$	$E_r$ is $E_r(aton)$	т – акат, тяр³.	.(OF							
Bond	Atom	-77	3	2	i	Final Total				1 200	ö	,	ļ		
		(eV)	કું	ું	\§.	Energy	<u></u>	<u> </u>	(S)	(eV)	. C	· ©	° •	(e, e,	, (a)
			7 puos	F puop	Bond 4	\$ (§	:	<u>:</u>	ring.	Final	:	:	>	•	Ē
Н,СО-Н	0	-0.82688	۰	•	۰		1,00000	0.86923	-15.65263		115.49	54.51	15.79	5 \$4605	27700
-H,C,O-H	0	-0.92918	٥	0	0		1.0000	0.86359	-15.75493		115.09	. 64.91	64.12	0.55182	0.36625
H,C-OH (C-O (j))	د	-0.82688	5	0		-152.44257	17716.0	0.86923	-15.63263	115.46177	96.59	19:41	46.30	1,21986	0.09981
H,C-OH (C-O (i))	0	-0.82688	o	o	۰		1.0000	0.86923	-15.65263	-	96.39	83.41	46.30	1.23926	0.09981
-H,C,-OH (C,-O (ii)	د.	-0.92918	-0.92918	0	0	-153.47405	0.91771	0,11549	-16,68411	-16.49325	93.09	16.38	43.59	1.29114	0.04398
-H <sub>1</sub> C <sub>*</sub> - OH (C - O (ii))	0	-0.92918	0	0	o		1.00000	0.86359	-15.75493		97,20	82.80	46.50	1,23692	0.10820
C-H (CH,)	υ	-0,92918	0	0	G	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
C-H (CH <sub>2</sub> )	C	-0.9291\$	-0.92918	0	0	-(53.47406	0,91771	0.81549	-16.68412	-16.49325	68.47	11.53	35.84	1,35486	0.29933
C-H (CH)	C	-0.92913	-0.92918	-0.92918	0	-154,40324	17710.0	0.77247	-17,61330	17.42244	61.10	118.90	31.37	1.42988	0.37726
$H_jC_iC_iH_jCH_j$ – $(C-C_i(a))$	C,	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-13.56407	63.82	116.18	30.08	1.83879	0,38106
$H_sC_sC_sH_sCH_s-(C-C^*(a))$	ر,	91526'0-	-0.92918	•	٥	-153,47406	0.91771	0.81349	16.68412	-16.49325	36.41	12.39	26.06	1,90890	0.45117
$R-H_1C_1C_1(H_2C_2-R_1)HCH_2-$ (C'-C'(b))	τυ	-0.92918	-0.92918	-0.92918	٥	-154,40324	17716.0	0.77247	-17,61330	-17,42244	<b>6</b> 50	131.70	21.90	1,97162	0.51388
$R - H_2C_4(R^2 - H_2C_4)C_4(R^2 - H_2C_7)CH_2 - (C - C^2(0))$	ď	-0.92918	-0 72457	-0.72457	-0.72457	-154.71860	17710	0,75889	-17.92866	ett.t1.71-	178	131.79	21.74	1.95734	0.50570
$koC_sC_s(H_sC_s-R^s)HCH_s-$ $(C-C_s(d))$	ť	-0.92918	-0.92918	-0.92918	0	-154,40324	17416.0	0.772A7	-17,61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$lenC_a(R-H_2C_s)C_b(R^n-H_2C_s)CH_2-$ $(C-C^n(e))$	ť	-0.72457	-0.72457	-0,72457	-0.72457	-154,51399	17118.0	0.76765	-17.92866	erttr.71-	\$0.04	129.96	2266	1.94462	0,49298
$lumC_{s,C_{s}}(H_{s}C_{s}-R^{s})HCH_{s}-(C^{s}-C^{s},0)$	ť	-0.72457	-0.92918	-0.92918	<b>ે</b>	-154.19863	17716.0	0,78155	-17,40869	.17.21783	52.78	127.21	24.04	1,9240	0.47779
$ ImC_{1}(R^{-}H_{2}C_{2})C_{4}(R^{-}H_{1}C_{2})CH_{3} -$	υť	-0.72457	-0.72457	-0.72457	-0.72457	-(54.51399	17716.0	0,76763	-17.92866	-17.73779	20.04	129.96	22.66	1 94463	0.49298

Jable 13.00. The effetty parameters (ev.) of full-difficults of di	CA OI INIMAIO	as From S of Gray	alkyl arcollols.			2	(0) )-)	(F) (F)	(9) 5-1	(P) (J-)	(J-)	(F)
l'arameters	Group	Graup	Godin	Groun	Gent.	Group	Group	Group	Group	Group	Group	Group
D,	-	-	_	3	2	-	-	-	1	1	1	-
n,	٥	0	o	2	-	0	0	0	0	0	0	0
a,	0	0	o	٥	٥	0	0	0	0	0	0	0
,;;	0.75	0.5	50	0.75	0.75	0,75	0.5	0.5	0.5	0.5	6.5	0.5
12.	_	-	-	-	-	-	-	1	1	1	1	1
, ,	0.75	-	-	-	-	-	1	1	1	ı	1	1
3	_	0.85395	0.85395	177160	17716.0	0.91771	17716.0	0,91771	0.91771	0.91771	17716.0	0.91771
6,	_	0	0	0	1	-	0	0	0	1	1	0
6.	_	2	3	_	-	-	2	2	7	2	2	2
, c,		0	0	3	2	ı	0	0	0	0	0 .	0
-,	0.75	0.5	0.5	0.75	0.75	57.0	0.5	0.5	5.0	0.5	0.5	0.5
	_	1	-	_	-	1	1	1	1	1	-	1
V, (aV)	-40.92709	-33.47304	-33,78820	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	14.81988	10,15605	10.19068	38.92728	25.78002	12,87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	16.18567	9.32537	9,47749	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	00506'9	6.90500
V. (aV)	-8.09284	4.66268	-4.73874	-1626957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(.w m) (eV)	-13.6181	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
Dinam (40 11) (41)	0	-1,65376	-1,85836	0	0	0	0	0	0	٥	0	0
$\mathcal{L}_{T}(\mu_{D} m)$ (cV)	-13.6181	-12.98113	-12.77653	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
(An) (orin)	-31.63247	-31,63544	-31.63529	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
Fr (atom - atom, msp', AO) (aV)	0	9/659,1-	-1,85836	0	0	0	-1.85836	-1,85836	-1,44915	-1.85836	-1.44915	-1.44915
Er (40) (cV)	-31.63537	-33.28912	-33.49373	-67.69450	-49.66493	-31.63537	-33,49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (1013 rad /.s)	44.1776	22,3978	12,2831	24.9286	24.2751	24.1759	9.43699	9,43699	15.4846	9,43699	9.55643	9.55643
Er. (aV)	29.07844	14.74264	8.08494	16.40846	15.97831	15.91299	621129	6.21159	10.19220	621159	6.2902.1	6.29021
En (aV)	-0.33749	-0.25287	-0.18841	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Erm (eV)	0,46311	0,12808	0.13328	0.35532 (Fo. (13.458))	0,35532 (Ea, (13,458))	0.35532 (Eq. (13.458))	0.1212 121	0.17978	0.09944	0.12312	0.12312	0.12312
<u>E</u> (aV)	-0.10594	-0.18883	-0.12177	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Em (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (towe) (aV)	-31.74130	-33.47795	-33.61550	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33,59732	-33.18712	-33.18712
Emmy (c, so no) (eV)	-13.6181	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emma (r. no no) (eV)	-13.59844	0	0	-13.59844	-13,59844	-13.59844	0	٥	0	0	0	0
$E_{p_j}(n_{mp_j})$ (dV)	4.41035	4.20817	4.34572	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.6	1. The total bond energies of a	alkyl alcohols ca	alculated using t	the functional gre	oup composition	n and the energ	ries of Table 1	15.60 compared	to the experime	ntal values (3)						
romuia	Formula Name OH C-O(i) C-O(ii) $CH$ , $CH$ $CH$ $CH$ $C-C$ (i) $C-C$ (i) $C-C$ (i) $C-C$ (i)	ŧ,	C-0()	C-0 (ii)	CH,	CH,	HO	C-C (a)	C-C (b)	ن-ن (9)	C-C (d)	(e) (j-)	(J-)	Coloniated		
	•		Group	Group		•		•	3				3	Total Bond	Experimental Total Rond	Ketative
CHO	Methanol	-	0	-	-		ļ							Energy (eV)	Energy (eV)	i
CHO	Ethanol	-	• •		- <b>-</b>	> -	<b>-</b> (	0	0	0	0	0	0	21.11038	21.131	0 00007
CHO	I-Propanol	_			· -		<b>5</b> 0	(	۰.	0	0	0	0	33.40563	33.428	990000
CHO	2-Propanol		• =		٠,	۹ ۵	۰ د	7	0 (	0	0	0	0	45.56333	45.584	0.00046
CHI	1-Butanol	-			٠.	> ^	- 6	7 (	۰ م		0	0	0	45.72088	45.766	0.00098
CHID	2-Butanol	_	. 0	٠.	- ^	۰ -	<b>-</b> -	n r	<b>5</b> 6	0 (	0	c	0	57.72103	57.736	0.00026
CHIIO OIII	2-Methyl-I-propananol	-	0		• ~			n c	<b>.</b>	٥,	0 4	0	0	57.87858	57.922	0.00074
CH <sub>II</sub> O	2-Methyl-2-propananol	_	0	-	<b>1</b> 1"	- c	- c	> 0	~ ·	0 1	0	0	0	57.79359	57.828	0,00060
CHIO	1-Pentanol	_		_	۰.	, ,	•	٠.	۰ د	<b></b> .	0	0	0	58.15359	58.126	-0.00048
C3H12O	2-Pentanol	_	0			• ^	> -	<b>#</b> •	۰ د	0 (	0	0	0	69.87873	69.887	0.0001
CsH120	3-Pentanol	-	. 0		• ^	۸ ر		<b>4 •</b>	۰ د	٥.	0	0	0	70.03628	70.057	0.00029
CHIO	2-Methyl-i-butananoi	_	0		, L	4 C		4 6	٥,	0 (	0	0	•	70.03628	70.097	0.00087
CHIO	3-Methyl-I-butananol		•		• ^	۰ د		7 -	<b>~</b> .	<b>.</b>	0	0	0	69.95129	69.957	0.00008
CHIO	2-Methyl-2-butananol	_	c		. ~	4	- c		<b>n</b> (		0	•	0	69.95129	09.950	-0.00002
C'Hio	3-Methyl-2-butananol	_	•		, ~	- د	٦ -	- «	۰ د	m ·	0	0	0	70.31129	70.246	-0.00092
CHT.O	I-Hexanol		0		. –		۹ د	<b>.</b>	ก่	٥,		0	0	18096'69	70.083	0.00174
O, H	2-Hexanol	_	•		. ~		<b>.</b>	٠.		۰.	•	0	0	82.03643	82.054	0.00023
CHIO	1-Heptanol	_	0	_	. –	· •	- c	, v	> 0	<b>-</b> (	0 (	0	0	82,19398	82,236	0.00052
C,H,D	I-Octanol	-	0			• [	> <	о г	-	o (	0	0	0	94.19413	94214	0.00021
CHIO	2-Ethyf-I-hexananol		. 0		- ^	. <u>c</u>	> -	٠	۰ د	0	0	0	0	106.35183	106,358	0.0000
CH	1-Nonzmol		. 0		• -	2 ∞	- c	4 0	m		0	•	0	106.42439	106,459	0.00032
Cuthio	1-Decanol	-	0				> <	• •	٥ د	٥,	0	0		118,50953	118,521	0,00010
CizHzo	I-Dodecanol	_	•			`=	> <	^ <u>-</u>	<b>&gt;</b> <	۰ (	0	0	٥	130.66723	130,676	0.00007
CI,H.O	I-Hexadecanol	-	0	_		· <u>v</u>	<b>,</b>	= =			٥,	φ.	•	154.98263	154.984	0.0000
							,	2	>		ا.	0	0	203.61343	203.603	-0.00005

.

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Exp. 0	O	101.53	(methand)	(cthand)	(ethanol)	107 (propanz)	112 (propens) 113.8 (butanc) 110.8	111.0 (butane) 111.4 (isobutane)				130.8 (isobutane)		111.4 (isobutane)	[11.4 (isoburane)	
Cal. 0	<u> </u>	72.50	1	106.78	110,17	108.44	110,49	110.49	08.601	109.44	109.44	110.67	110.76	111,27	111.27	
_	.©															
9	·©															L
9	.©						12.69	69.31		10.56	70.56					
E.	(§)		>	-	•1.63376	0	i		0			-1.\$5836	0	0	-1,25836	
,,				0.91771	0,83472	1,15796			9625171 .			0.81549	1.04887	1.04887	1.04827	
3	-		,,	£7.0		0.75			0.75			1	87.0	6.75	\$2.0	
Ü	; ;			-	1	. 1			1			1	1	1	1	
Ü	7		6.73	0.75	1	1			1			1	6.75	0.75	6.75	
3	Atm 2		17160	17716.0	0.85395 (Eq (15.114))	-						0.81549	0.91771	0.91771	0.91771	
	Abril 1		-	1	0.81549	0.86359			0.86359			0.81549	0.87495	Q.87495	0.87495	
Arom 2	Hybridization Designation	(Table  5.3.A)	•	1	0	×			in.			13	1	-	-	
12	Airm 2		-14,163.13	-14.82575	-13 61806	=			н			-16.68412 C.,	-14.82575 C.	-14,82375 C,	-14,82575 C,	
Aforn 1	Hybridization Designation	(Table 15.3,A)	-	-	ฆ	1			7			25	\$	~	\$	
Li,	Alem J		-14,82575	-14,82575	-16.68412	-15,73493			-15,75493			.16.68412 C.	-15.55033	-15,55033	-15,55033 C,	
1,2%	Tombal Alone $(a_0)$		7,6697	3,6515	4.5826	3.4252			3.4252			4 7958	4 (633	4 1633	4 7058	
3	(a)		3916	1.83616	2.67024	2,11106			1.1700.1			29 547	21133	2,09711	2,90327	
2,5	<u>6</u>		267935	267024	29(547	2,11106			2,09711			291547	2,91547	291547	2,90327	
Atomate/Auge   2c   3c   2c   C   C   C   C   C	•	НО.37	(0, 0-0)	((j) ()-'.)) H(j'.)7	(C, -0 (ii)	Mathebas ZHC: H	"ענ'פ'ננ"	H'.5.77	Medy!	7,7,7,77	H*5.77	") *** "C"C"C"	LC,C,H in C,	<i>AC,C,H</i> ₩ C,	ZC,C,C,	

ETHERS  $(C_n H_{2n+2} O_m, n = 2,3,4,5...\infty)$ 

The alkyl ethers,  $C_n H_{2n+2} O_m$ , comprise two types of C-O functional groups, one for methyl or t-butyl groups corresponding to the C and the other for general alkyl groups. The alkyl portion of the alkyl ether may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the 10 isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in ethers are equivalent to those in branched-chain alkanes.

Each C-O group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO 15 and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ethers, the C2sp3 HO has a hybridization factor of 0.91771 (Eq. (13.430)) and an energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the O AO has an energy of  $E(O) = -13.61806 \, eV$ . To meet the equipotential condition of the union of the C - O  $H_2$ type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_1$  of Eq. (15.52) for the 20 C-O-bond MO given by Eq. (15.113) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ .  $E_r(atom-atom, msp^3.AO)$  of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is  $-1.44915 \, eV$  for the  $CH_3 - O -$  and  $(CH_3)_3 \, C - O -$ C-O groups. It is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), and the  $C2sp^3$ 25 HO of a methyl group as given by Eq. (14.151). For the alkyl C-O group,  $E_r(atom-atom, msp^3.AO)$  is -1.65376 eV. It is based on the energy match between the O AO and the  $C2sp^3$  HO of a methylene group and is given by the linear combination of -0.72457 eV (Eq. (14.151)) and -0.92918 eV (Eq. (14.513)), respectively.

The symbols of the functional groups of branched-chain alkyl ethers are given in Table 15.63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl ethers are given in Tables 15.64, 15.65, and 15.66, respectively. The total energy of each alkyl ether given in Table 15.67 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.66 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl ethers determined using Eqs. (15.79-15.108) are given in Table 15.68.

of alkyl ethers.	Group Symbol	0-0	(£) 0 - 0	C-H (CH)	(t) (H) H-D	(cu);	#10	(a) 0 1 0 1 0 1 0 1 0 1 0 1 0 1 0 1 0 1 0	(a) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	(e) (c) (c)	(a) (c) (d)	(e) (e) (l) (l) (l) (l) (l) (l) (l) (l) (l) (l
Table 15.63. The symbols of functional groups of alkyl ethers.	r unctional Group	C-O $(CH_3 - O - \text{ and } (CH_3), C - O - )$	C-O (alkyl)	CH, group	CH <sub>2</sub> group	CH	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (t to t-C)	CC (t to iso-C)

Table 15.64.	Table 15.64. The geometrical bond parameters of alkyl ether	meters of alkyl ethers and exp	rs and experimental values [1]								
י פו פווזכונו	(E) all (E)	(ii) C-0	C-H (CH.)	C-H (CH.)	C-H	(a) <u>C</u> =C		0			
	4	Croup	Group	Group	Group	Group	Group Group	(S)	(g) 	(e) C-C (e)	2-2
a (a <sub>0</sub> )	1.80717	1.79473	1 64920	1 67177				droin	dnoro	Group	Group
c, (a)	1 24421			771/01	1.0/465	2,12499	2.12499	2.10725	2 12490	2 10.00	
(0.)	1.3445.1	1.33968	1.04856	1.05553	1 05661	1 15711			///	67/01.7	2.1072
Bond					TOOCO'T	1.45/44	1.45744	1.45164	1.45744	1.45164	1.4516
2c' (A)	1.42276	1.41785	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1 54780	1000	
Eva Dand			1 101							CC0CC-1	1.5363.
Length	1,416	1.418		1.10/ (C~H		1.532	1.532	1.532	1530	1 637	
<u> </u>	(dimethyl ether)	(ethyl methyl ether (avg.))	,	propane)	(isobutane)	(propane) 1.531	(propane) 1.531	(propane)	(propane)	(propane)	L.S32 (propane
b.c (a.)	STEAL I		(C-H butane)	(C-H butane)		(butane)	(butane)	(butane)	(butane)	(hittane)	1.53
	97707.1	1.19429	127295	1.29569	1 20024	1 54610			,	(comme)	(on rane
0	0.74388	0.74645	00000		17667	010401	1.54616	1.52750	1.54616	1 57.750	1
			-					-		7777	7

Table 15.65. The MO to HO intercept geometrical bond parameters of alkyl others.	trical bond	parameters of all	yl ethers. R.R.	R.R., R. are H or alkyl groups.		$E_{r}$ is $E_{r}(alom-alom,msp^{*}AO)$	nom.msp*AO)								
Bond	Atom	E, (eV)	(eV) Bond 2	E, (eV) Bond 3	Er (eV) Bond 4	Final Total Energy (72xp²	J ©	J (g	Final	E(C2xp³) (eV) Final	<b>6</b> ©	, (°)	θ	(a,)	(g) 4.
						83			1	+	1	1	1		T
('-H (M; H,)	٠.,	TSM2T.O.	0	e	0	152.34026	0,91771	0,87495	-15.55033	15,35946	3.5	101.15	42.40	ווודו	0,16921
H,C, -0-C,H, (CH,),C, -0-C,H, (CH,),C, -0-C,(CH,), (C-O, W)	ئ	4.72457	0	c	0	-152.3402K	0.91771	0.87495	:15.58033	.15,35946	¥0.29	8	46.10	1.25319	0,09112
H.C O - C.H. (CH.), C O - C.H. (CH.), C O - C. (CH.), (C - O 6)	o	-0.72457	-0,73457	0	0		1.00000	0.13600	-1627490		22.66	¥5.78	43.74	1.30535	0,03876
$-H_1\zeta_a - O\zeta_s(CH_s)_s$ $-H_1\zeta_a - O\zeta_sH_s$ $(C-O\ (ii))$	u'	-0.82688	-Q.9291R	0	0	5717£ 851-	17710	0.82653	16.58181	-16.39095	177	87.39	43.33	1,305.1	0.03456
-H,C,-OC,(CH,), -H,C,-OC,H, (C-O (ii))	0	-0.72457	-0, я2сяв	U	0		1.0000	0.83078	05277291-		13.33	16.67	43.98	1.29138	0.04829
-H <sub>1</sub> C, -0-H <sub>1</sub> C, -	0	-0,¥26 <b>28</b>	-0.K2GKK	0	0		1.00000	0.12562	-16,47951		92.87	87.13	43.66	1.29229	0.04138
C-H (CH,)	i	.0.92918		-	•	-152.34487	0.91771	0,16359	-15.75493	-15,56407	77.49	10201	41.48	1,23564	0.18708
C-H (CH;)	Ü	-0.92918	-0.92918	0	o	-153,47406	17716.0	0,81549	-16.61412	-16.49325	68.47	111.53	33.84	135486	0.29933
C-H (CH)	ر	-0,92918	-0.92918	-0.92918	0	-154.40324	0.91771	0,77247	-[7,61330	-17,42244	61.10	618.30	11.37	1,42988	0.37326
H,C,C,H,CH,	U	.0,9291¥	0	a	0	1175.221-	0.91771	0.86359	-15,75493	-15,36407	63.82	116.18	30.08	1.83879	0.38106
H,C,C,H,CH <sub>3</sub> -	ű	-0.92918	-0,9291R	٥	0	90141/8511	17710.0	0.81549	-16.68412	-16.49325	S£41	123.59	25.06	1.90290	0.45117
$(R - H_2C_{-1}C_{+1}(H_3C_{+1} - K^{-1})HCH_2 - K^{-1}C_{+1}C_{+1}$	ن	#1626'D-	-0.92918	#1629.t <del>/</del>	0	154.40324	17716.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_a(R' - H_2C_a)C_a(R^a - H_2C_a)CH_3 - CCH_3 - CCH_3$	ئ	-0,92918	-0.72457	-0.72457	4.72457	09812'851-	17716.0	0.75889	-17.92166	97,57,51.	48.21	62.161	21.74	1,95734	0.505.0
$kaC_{s}C_{s}(H_{2}C_{s}-R)HCH_{3}-HC_{s}C_{s}(H_{3}-H)C_{s}(H_{3}-H)C_{s}(H_{3}-$	ن	-0.92918	-0.92018	-0,92918	•	-154,40324	17716.0	לצבירו.0	-17.61330	-17.42244	48.30	07.161	21.90	29116.1	0.51388
urk" (R-H;C.)C. (R"-H;C.)CH;-	ť	-0.72457	-0.72457	-0.72457	-0.72657	66818.421.	0.91771	0.76765	-17.92866	-17.73779	\$0.04	129.36	22,66	1.9462	0,49208
IENG'S; (H.C R.) HCH; -	ť	4,73.57	40.92918	-0.92918	-0	-154,19863	17716.0	0.78155	-17.40869	-17.21743	52.78	17.73	P) ZZ	1.92443	0.47779
$linC_{*}(R-H_{2}C_{*})C_{*}(R^{*}-H_{3}C_{*})CH_{3}-$	ئ	-0.72457	-0.72457	-0.72457	72.02-	-154.51399	17710.0	0.76765	-17.92866	-17.73779	30.04	129.96	22.66	1,94462	0.49298

Table 15.66. The energy parameters	(cV) of functions	al groups of alkyl	cthers.				1	17, 17	17.0	(3)	6,000
Parameters	C-0 (i)	(11) 0-2	(.11,	÷.	H)	(a)	Grans	Group Group	Grade	danous C	danoub
	Group	Group	Group	Group	dio 15	1					-
17	-	-	m	2	_	-	-	-	-	-	Ţ
		6	2	-	0	٥	0	0	0	0	۰
	, ,		-	•	0	۰	0	0	0	0	0
·6		, ,	32.0	0.75	0.73	0.5	0.5	0.5	0,5	0.5	0.5
<u>.</u>	çj.	3 -	-	-	-	-	_	1	-	1	1
	- -	1		-	-	-	-	-	-	1	1
C.	-	- 1000	100	122100	122100	12210	177160	17716.0	0.91771	0.91771	0.91771
· S	0.83395	0.83393	0.9171	1,1,1	-	6	G	٥	-	-	٥
5	٥	• .			-	7	2	2	2	2	2
Ü	7	7	-		-   -		-	c	•	0	0
Ů.	0	٥	,	,		,	,		•	50	0.5
,,,	0.5	0.5	0.75	6.75	0.75	65	3	3	-	-	-
	-	~	1	-	-	-	-	-			
v (eV)	-33.15757	-33.47304	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	29.101.62	23,101.62
7 (27)	10,12103	10.15605	38.92728	25.78002	12.87680	9,33352	9.33352	9.37273	9.33352	9.37273	9.37273
1.7.7	017780	0 12417	32 53914	21.06675	10,48582	6.77464	6.77464	6,90500	6.77464	6.90500	6.90500
(36) 7	4 58605	4 66768	-16.26957	-10,55337	-5.24291	3,38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
(40)	0892971	-14 63489	-15 56407	-15,56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15,35946	-15,35946
AF (mm) (aV)	-1 44915	0,165370	•	0	0	0	0	0	0	0	0
ייין נייין נייין נייין נייין נייין	12001	12 00 113	15 46407	-15 \$6407	-14.63489	.15.56407	-15.56407	-15.35945	-15.56407	-13.33946	-15.35946
(a) (a) (a)	-15,105/4	21 62544	67 69451	49,66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	-31,63535
12 (18, val (ev)	1 44015	7,1647	G	0	0	-1,85836	-1.83836	-1,44915	-1.85836	-1.44915	-1,44915
Table of the state	22,00463	22 39013	03 404 57	40 66493	-31.63537	-33,49373	-33.49373	-33.08452	-33.49373	-33,08452	-33,08452
(10) (cr.)	12 0329	12.1583	24.9286	24,2751	24.1759	9,43699	9.43699	15.4846	9.43699	9,55643	9.55643
(2) (2) (2) (2) (3) (4) (4) (4) (4) (4) (4) (4) (4) (4) (4	7 02028	8.00277	16.40846	15.97831	15.91299	6.21159	6,21159	10,19220	651129	6.29021	6.29021
(10) Y	0.18470	-0.18631	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0,20896	-0.16515	-0.16416	-0.16416
Ext. (cV)	0.13663	0.16118	0.35532	0.35532	0.35532 (Fq.(13.458))	0.12312	0.17978	0.09944	6.12312 [2]	0.12312 [Z]	0.12312 [2]
Q-7	011580	22501 0	-0 22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
(c) (c)	0 14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E 1-1 (aV)	.33,20040	-33 39484	-67.92207	-49.80996	-31.70737	-33,59732	-33.49373	-33.24376	-33.59732	-33,18712	-33.18712
( ) ( ) ( )	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
F ( 40 m) (cV)	0	0	-13.59844	-13.59844	-13,59844	0	0	0	٥	0	0
T. (-) (-)	\$ 93062	4.12506	12.49186	7.83016	3,32601	4,32754	4,29921	3.97398	4.17951	3.62128	3.91734

1 8DIC 13.0	able 13.07. Inc total bond energies of tilkyl emers calc	3	ed using the fun	sied using the functional group composition and the energies of Table 15.66 compared to the experimental values [3]	SIMPOSITION BILL	d the energies o	of Table 15,06	compared to the	experimental y	alucs [3].					
Formula	Name	(i) O-2	(H) 0-2	С.Н.	CH.	H.)	(B)	[ <del>q</del> ]	(a) .)—.)	(E) (C)	(E)	C-C (6)	Calculated	Experimental	Relative
		Ç	Grand		•							;	Total Bond	Total Bond	Emer
													Energy (eV)	Energy (aV)	
C'HEO	Dimethyl ether	7	0	~	•	•	•	•	0	o	0	0	32,84496	31.901	0,00174
o E	Ethyl methyl ether	_	_	۲4	-	0	-	0	0	0	0	0	45,19710	45.183	-0.00030
O E	Diethyl ether	0	7	~	7	•	~	•	٥	0	0	0	57,54924	57.500	-0,00086
Q H	Methyl propyl ether	_	_	7	7	•	7	٥	٥	0	0	0	57,35480	57.355	0,0000
O X	Isopropyl methyl either	_		•	•	-	0	7	0	0	0	0	57,45569	57.499	0.00075
O'H''	Dipropyl cilver	0	7	~	4	•	*	0	٥	0	0	•	81.86464	81.817	-0.00059
O,H,O	Diisopropyl ether	0	**	v	0	7	0	₫	o	0	0	٥	82.06642	83.088	0,00026
ב האלים	(-Butyl ethyl ether		-	77	_	•	-	٥	•	0	0	•	82,10276	82.033	-0,00085
O'H'U	t-Butyl isopropyl ether	_	_	٠,	0	-	0	63	_	•	0	0	94,36135	94.438	0,00081
O H	Dibutyl ether	0	~	77	9	•	9	0	0	0	0	•	106.18004	106.122	-0.00055
O.H.	Di-sec-butyl either	0	7	•	~	-	~4	4	•	0	0	0	106.38182	106.410	72000.0
Q i	Di-t-butyl other	~	0	•	•	0	0	•	•	0	0	•	106.65628	106,425	-0.00218
O. E.	r-Buryl soburyl ether	-	_	٠,	-	_	-	~	_	0	0	•	106 49077	106.407	20000

Table 15.68. The bond angle parameters of alkyl ethers	alkyl ethers	and experim	ental values [1]. In	the calculat	and experimental values [1], in the calculation of $ heta$ , the parameters from the preceding angle were used. $E_r$ is $E_r$ (onton – atom, msp $ AO angle$ )	Inctors from th	se preceding a	ngle were u	ed. E <sub>7</sub> is	Er(alom -	dom, msp	(a).			:		
2c' Tembei Arra (a,)		Frank Atra I	Atom ( Hybridization Designation (Toble 15.3.A)	// nate	Aton 1 Hybridization Designation (Table 13.3.A)	2 <sup>5</sup> 1	C <sub>2</sub> Anns 3	j.	ر."	6-	٧.	Ε <sub>τ</sub> (aV)	9,0	e. ©	(C)	9 E	gi⊙
- 1225	<u> </u>	-17,40869	E,	-17.40869	25	0.78155	0.74135	-	-	-	0.72155	-1.85836				11.24	(dimethy)
4,4385		-17.51099	÷	-17.51099	Ŧ	0.77694	0,77699	-	-	-	0,77699	-1.45R36				111.35	111. (cthyl med)
43607	_	-16.68413	25	90819 61-	o	0.81549	0,83393 (Eq. (13,114))	-	-	-	D,83472	-1.65376				100113	(caby) methy
3,4252	-	-15,75493	7	æ	τ	0.86359	-	-	1	6.75	1.15796	0				108.44	Of ethod)
·													15.60			110.49	(proper 113. Pudes (prodes)
													69.51			110.49	Guta 11.
3,4252		-15,75403	1	I	н	0,86359	1	-	-	0.75	1.15736	o				109.50	
													70.56			4.00	
													70.56			103.44	
4.7933		-14,61412 C.	25	-16.68412 C.	z	0.81349	0.81549	-	-	•	0.81540	-1,85836				110.67	(isobas
4,1633		-15.55033 (',	5	-14.82575 C.	ı	0.87495	11116.9	6.75	-	0,75	1.04887	°				110.76	
4.1633		.15,55033	3	-14.82575 C*		0.87495	0,91771	0.75	-	a.75	1,04897	0				111	(Geobera
4.795R		*.)	3	-اط.22375	_	0.87495	1,7110,0	0.73	-	0.75	1.04887	-1.85836				111.27	111. Gsobut

PRIMARY AMINES 
$$(C_n H_{2n+2+m} N_m, n=1,2,3,4,5...\infty)$$

The primary amines,  $C_n H_{2n+2+m} N_m$ , comprise an  $NH_2$  functional group and a C-N functional group. The alkyl portion of the primary amine may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and 5 methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in primary amines are equivalent to those in branched-chain alkanes.

The primary amino  $(NH_2)$  functional group was solved using the procedure given in the Dihydrogen Nitride  $(NH_2)$  section. Using the results of Eqs. (13.245-13.368), the primary amino parameters in Eq. (15.52) are  $n_1 = 2$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)), 15  $C_{10} = 1.5$ , and  $c_1 = 0.75$ . In primary amines, the  $C2sp^3$  HO of the  $C - NH_2$ -bond MO has an energy of  $E(C,2sp^3) = -15.35946 \, eV$  (Eq. (15.18) with s = 1 and Eqs. (15.19-15.20)) and the N = 1 AO has an energy of  $E(N) = -14.53414 \, eV$ . To meet the equipotential condition of the union of the N = 1 H<sub>2</sub>-type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  of Eq. (15.52) for the N = 1-bond MO given by Eq. (15.68) is

20 
$$c_2(H \text{ to } 1^\circ N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.35946 \text{ eV}} = 0.94627$$
 (15.115)

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In primary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a 25 corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the N AO has an energy of  $E(N) = -14.53414 \, eV$ . To meet the equipotential condition of the union of the

C-N  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C-N-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2\left(C2sp^3HO\ to\ N\right) = \frac{E(N)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-14.53414\ eV}{-14.63489\ eV}(0.91771) = 0.91140 \quad (15.116)$$

 $E_T(atom-atom, msp^3.AO)$  of the C-N-bond MO in Eq. (15.52) due to the charge donation 5 from the C and N atoms to the MO is  $-1.44915 \, eV$ . It is based on the energy match between the N of the  $NH_2$  group and the  $C2sp^3$ . HO corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups,  $-0.72457 \, eV$  (Eq. (14.151)), where the N-H bonds are also energy matched to the C-N bond.

The symbols of the functional groups of branched-chain primary amines are given in Table 15.69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of primary amines are given in Tables 15.70, 15.71, and 15.72, respectively. The total energy of each primary amine given in Table 15.73 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.72 corresponding to functional-group composition of the molecule. The bond angle parameters of primary amines determined using Eqs. (15.79-15.108) are given in Table 15.74.

Table 15.69. The symbols of functional groups of primary amines.

Table 15.09. The symbols of	functional groups of primary a
Functional Group	Group Symbol
NH <sub>2</sub> group	NH <sub>2</sub>
C-N	C-N
CH₃ group	$C-H(CH_3)$
CH₂ group	$C-H(CH_2)$
СН	C – H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

20.00	able 10.70. The geometrical bolid parallicity of prin									Annual Control of Cont	-
Parameter	NH.	٥-٦	C-H(CH)	C-H (CH.)	H-3	(, -(, (a)	C-C (b)	(e) C~C (e)	C-C (d)	(e) 2-2	(i) :>-::
	Group	Group	Group	Growip	Group	Group	Group	Group	Group	Group	Group
a (o°)	1.28083	1,92682	1.64920	1,67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c' (g,)	0.95506	1.38810	1.04856	. £5550*1	1.05661	1.45744	1,45744	1.45164	1.45744	1,45164	1.45164
Bond Longth 2c' (A)	1.0108	1,46910	1.10974	81711.1	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Fvn Rond			1,107	1.107		1.532	1.532	1.532	1.532	1.532	1.532
Length	1.010 (methylamine)	1.47! (methylamine)	(د	Ն	1.122 (isobutane)	(propane) 1.531	(propane)	(propane) 1.531	(propane) 1.531	(propane) 1.531	(propage) 1.531
₹)			(C-H butane)	Š		(butane)	(butane)	(butane)	(buttane)	(butane)	(butane)
h,c (a,)	0.85345	1.33634	1,27295	695671	1.29924	1.54616	1.54616	1.52750	1,54616	1.52750	1,52750
u	0.74566	0.72041	0.63580	0.63159	0,63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.71. The MO to HO intercept geometrical bond parameters of primary smines. $R,R',R''$ are $H$ or alkyl groups. $E_p$ is $E_p$ (alom – alom, myr) $AO$	strical bond	parameters of p	rimary amines.	R,R',R" are H	or alkyl groups	$E_r$ is $E_r(ala)$	m - atom, myr	,40).							
Bond	Atom	£7	1,7	18,7	Er	Final Total	,	1,624	Erratura	$E(C2sp^2)$	.6	6	9	ď	Α,
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy ('2'y <sup>2</sup> '	(°)	(°)	(eV) Final	(eV)	<u> </u>	©	E	(°b)	(%)
H,CN(H)-H	2	-0.72457	0	0	٥		0.93084	0,87495	-15,55033		118.00	62.00	64.83	0.54432	0.41075
-H,C,N(H)-H	2	-0.72457	0		۰		0.93084	0.87495	-15,55033		118.00	62.00	64.83	0.54432	0.41073
H,C-NH,	U	-0.72457	0	٥		-15234026	0.91771	0 87495	-15.55003	-13.35946	85.28	11.76	40.73	1.46010	0.07200
H,C-NH,	2	-0.72457	٥	٥	0		0.93084	0.87495	-15.55033		85.28	54.72	40.73	1.46010	0,07200
-H <sub>2</sub> C, -NH <sub>1</sub>	ن	-0.72457	81626.0-	٥	٥	-153,26945	0,91771	0.82562	-16.47951	-16.28864	80.20	08'66	37.50	1,52858	0.14043
-H,C, - NH,	2	-0.72457	•	0	0		0.93084	0.87495	-15.55033		85.28	24.72	40.73	1.46010	0.07200
C-H (CH,)	د	81620.0-	0	0	0	-152.54487	17716.0	0.86359	-15.75493	-13.56407	77.49	15.201	41.48	1,23564	0.1870\$
C-H (CH <sub>2</sub> )	Ü	B1626.0-	-0.92918	•	۰	-153,47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
C-H (CH)	U	40.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	11,37	1,42988	92577.0
H <sub>3</sub> C <sub>2</sub> C <sub>3</sub> H <sub>2</sub> CH <sub>3</sub>	O,	81626.0	0	0	0	-132.54487	0.91771	65£98.0	-13.75493	-13.56407	63.82	116.18	30.08	1.83879	901850
H,G,C,H,CH,	ť	-0.92918	-0.92918	0	0	-133,47406	a91771	0.81349	-16.58412	-16.49325	\$6,41	85.031	26.06	1.50890	0.45117
$R - H_2^{-1}C_2(H_2^{-1}C_2 - R)HCH_2^{-1}$	ਹ	81622.0-	£1626.0-	-0 92918	0	-154,40324	177160	74277.0	17.61330	-17,42244	48.30	06.181	21.90	191161	0.51388
$(R - H_1C_*(R' - H_1C_*)C_*(R' - H_2C_*)CH_1 - (C - C_*(C))$	ڻ	-0.9291B	-0.73¢57	-0.72457	-0.72457	-154.71860	a 91 77 J	0.75889	-17.92866	-17.77	48.21	131.79	21.74	1,95734	0.30370
$isoC_{iC_{i}}(H_{i}C_{i}-R^{i})HCH_{i}-(C-C_{i}(d))$	ີ :	81626'0-	81626'0-	81626'0-	0	-154,40324	0.91771	72277.0	-17,61330 .	-17,42244	48.30	131.70	21.90	29116.1	0.51388
$lenC_{\sigma}(R^{n}-H_{2}C_{\sigma})C_{\kappa}(R^{n}-H_{2}C_{\sigma})CH_{2}-$ $(C-C_{\sigma}(C))$	ن '	-0.72457	-0.72457	LS\$7L'0-	-0.72457	-(54.5)399	0.91771	0.76765	-17.93866	-17.73779	50.04	129.96	22.66	1,94462	0.49298
(C-C; (b))	່"ວ	-0.72457	-0.92918	81676'0-	ಕ	-154.19463	0.91771	0,78155	-17,40869	-17.21783	52.78	127.22	24.04	1,92443	0.47279
$imC_{*}(R'-H_{*}C_{*})C_{*}(R''-H_{*}C_{*})CH_{*}-$ (C-C;(0))	τ'	-0.72457	72457.0-	-0.72457	-0.72457	-154.51399	17718	0,76765	17.92866	errer.r1-	\$0.04	129.96	22.66	1,94462	0.49298
							!		:						

Parameters	NH,	2 eg	Group C'H,	 # #	Grand Grand	Group Group	Group Group	Group Group	Gode (5)	Close of	Group
	Orden p	-	3	2	-	_	-	1	1	-	-
	6	G	2	-	0	0	0	o	0	0	o
	1	0	0	0	•	٥	0	0	o	0	0
	0.75	20	0.75	0.75	0.75	5,0	0.5	5.0	5'0	0.5	0.5
	0.93613	-	-	-	-	-	1	1	1	1	-
3	0.75	-	-	-	-	-	1	1	1	1	1
8	0.94627	0.91140	171160	0.91771	17710.0	17716.0	177160	17716.0	17716.0	0.91771	17716.0
2,	0	0	°	-	-	o	0	0	1	1	o
ς,	-	2	_	-	-	Cŧ	7	7	2	2	2
	2	0	3	2	-	0	o	o	0	0	0
	1,5	0.5	0.75	0.75	0.75	20	0.5	٥.5	50	6.5	0.5
	-	-	-	-	-	-	-	1	1	1	ı
V (cV)	-77.89897	-32.46339	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.101.12	-29.10112
V. (eV)	28.49191	9.80175	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
7. (al/)	30.40957	8,42409	32,53914	21,06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (cV)	-15.20478	-4.21204	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(*1 m) (aV)	-14.53414	-14.63489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15,56407	-15,35946	-15.35946
15 (V) m) (aV)	0	-1,44915	0	0	0	0	0	٥	0	0	0
E. (20 m) (0V)	-14.53414	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
E(1, 40 10) (4V)	-14.53414	0	0	0	۰	0	0	0	0	0	0
L. (u, m) (eV)	-48.73642	-31,63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31,63535	-31,63537	-31,63535	-31.63535
E. (atom - atom, myp3, AO) (eV)	0	-1,44915	0	0	0	-1.85836	-1,85836	-1.44915	-).85836	-1,44915	-1.44915
E. (w) (eV)	-48.73660	-33.08452	-67.69450	-49.66493	-31,63537	-33.49373	-33,49373	-33.08452	-33.49373	-33.08452	-33.08452
@ (10 <sup>13</sup> rad / x)	64.2189	18.9231	24.9286	24,2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E. (cV)	42.27003	12,45552	16.40846	15.97831	15.91299	6.21159	65112.9	10.19220	6.21159	6.29021	6.29021
E. (cV)	-0.40690	-0.23100	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Eras (aV)	0,40929	0.12944	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,35532 (Eq. (13,458))	0.12312	0.17978 [4]	0.09944 [5]	0.12312	0.12312	0.12312 [2]
E (cV)	-0.20226	-0.16628	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
£ (aV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Erking) (cV)	49.14112	-33,15079	-67.92207	-49.80996	-31.70737	-33.59732	-33,49373	-33.24376	-33_59732	-33.18712	-33.18712
E (4. 10 10) (aV)	-14.53414	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	14,63489	-14.63489	-14.63489	-14.63489
E(n.0.10) (aV)	-13.59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0

(e) C-C 

				1			$\overline{}$	$\overline{}$	$\overline{}$					_
_	<u> </u>	107.1 (methylamine	110.3 (methybanine	(methylamine ) 107 (untowne)	(propens) 113.8 (butane) (forbarne)	(butants)	ia manage			110.8 (isobatane)		111.4 (isobutane)	111.4	francisco anna
<u>15</u>	C	108.40	110.48	108.44	110.49	110.49	109.50	109.44	109.44	110,67	110.76	111.27	111.27	
8	<u>.</u>		L											
9	T ©													
6	·C				15,89	69.51		70.56	70.56					
. [	(eV)	۰		. 0			0			-1,83836	a	c	-1.85836	
Atomic C. C. C. C. C. C. C. C.	•	1.05679	0.97194	1.15796			1.15796			0,81549	1.04887	1.04887	1.04887	
	<u>.</u>	67.0	6.73	0.75		·	0.75			_	0.75	0.75	0.75	
Š	•	-	-	 -			-			-	-	-	-	
Ü	•	-	27.0	-			-			_	0.73	£.0	27.0	
5	Atom 2	1	0.88583	-			-			0.81549	17716.0	0,91771	17716,0	
5	I metV	0.94627 Eq.(15.115)}	0.91140 (Eq. (15.116))	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
Atom 2 Hybridization	Designation (Table 15.3.A)	н	z	<b>H</b>			н			ล	_	_	-	
E. mines	Atem 2	Ŧ.	-15,35946	x			x			-16.68412 C.	-(4.82575 C,	-(4.82575 C.	-14.825	Ī
Atom i Hybridization	Designation (Table (5.3.A)	z	3				7			Ħ	s	8	\$	<u> </u>
E's manual	or F.	-14.53414	-14.53414	-13.73493			-15.75493			-10,08412 C,	-13.35033 C.	-13.55033 C.	-15,55033 C <sub>4</sub>	Ī
2c'	Monte ( Q, )	3.0924	3.8816	3,4252			3,4252			4.7958	4.1633	4,1633	4.7958	
2¢'	(a,)	(1.91013	2.77620	211106			2.09711			2.91547	2,11323	11700.2	2.9027	
2c' Bond I	(a,)	1.91013	1.91013	2.11106			2.09711			2.91547	2.91547	2.91547	2.90327	ľ
Alabia of Angla		HNH7	CHNC.	Mah kar ZHC_H	'.''C'''.	H,C,C,H	Н. ЭНС	7,7,7	U' 5' 77	, , , , , , , , , , , , , , , , , , ,	, ZC,C, H == C,	ZC,C,H ₩.C,	40,5°,C, ۳۹ C,	5.7.77

## SECONDARY AMINES $(C_n H_{2n+2+m} N_m, n=2,3,4,5...\infty)$

The secondary amines,  $C_nH_{2n+2+m}N_m$ , comprise an NH functional group and two types of C-N functional groups, one for the methyl group corresponding to the C of C-N and the other for general alkyl secondary amines. The alkyl portion of the secondary amine may 5 comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in secondary amines are equivalent to those in branched-chain alkanes.

The secondary amino (NH) functional group was solved using the procedure given in the Hydrogen Nitride (NH) section. Using the results of Eqs. (13.245-13.316), the secondary 15 amino parameters in Eq. (15.52) are  $n_1 = 1$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)),  $C_{1o} = 0.75$ , and  $c_1 = 0.75$ . In secondary amines, the  $C2sp^3$  HO of the C-NH-bond MO has an energy of  $E(C,2sp^3) = -15.56407 \, eV$  (Eqs. (14.514-14.516)); Eq. (15.29) with s=1 and s=2, Eq. (15.31), and Eqs. (15.19-15.20)) and the N AO has an energy of  $E(N) = -14.53414 \, eV$ . To meet the equipotential condition of the union of the N-H  $H_2$ -20 type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  of Eq. (15.52) for the N-H-bond MO given by Eq. (15.68) is

$$c_2(H \text{ to } 2^{\circ}N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.56407 \text{ eV}} = 0.93383$$
 (15.117)

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the 25 N AO to form a MO permits each participating orbital to decrease in radius and energy. In secondary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the N AO has an energy of  $E(N) = -14.53414 \, eV$ . To meet the equipotential condition of the union of the

C-N  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C-N-bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ .

As given in the Continuous-Chain Alkanes  $(C_nH_{2n+2}, n=3,4,5...\infty)$  section, each methylene group forms two single bonds, and the energy of each  $C2sp^3$  HO of each  $CH_2$  group 5 alone is given by that in ethylene,  $-1.13379 \, eV$  (Eq. (14.511)). In secondary amines, the N of the NH group also binds to two  $C2sp^3$  HOs and the corresponding  $E_T(atom-atom, msp^3.AO)$  of each C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is  $-1.13379 \, eV$ . It is based on the energy match between the N of the NH group to the two  $C2sp^3$  HOs corresponding to the energy contributions to each of the two single bonds 10 that are equivalent to those of independent methylene groups,  $-1.13379 \, eV$  (Eq. (14.511)), where the N-H bond is also energy matched to the C-N bonds.  $E_T(atom-atom, msp^3.AO)$  of the C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is  $-1.13379 \, eV$ . It is based on the energy match between the N of the NH group to two  $C2sp^3$  HOs corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups,  $-0.72457 \, eV$  (Eq. (14.151)), where the N-H bonds are also energy matched to the C-N bond.

The symbols of the functional groups of branched-chain secondary amines are given in Table 15.75. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of secondary amines are given in 20 Tables 15.76, 15.77, and 15.78, respectively. As in the case of  $NH_2$  (Eq. (13.339)),  $C_{1o} = 2C_1$  rather than  $C_{1o} = C_1$  in Eq. (15.52) for the C - N bond. The total energy of each secondary amine given in Table 15.79 was calculated as the sum over the integer multiple of each  $E_D$  (Group) of Table 15.78 corresponding to functional-group composition of the molecule. The bond angle parameters of secondary amines determined using Eqs. (15.79-15.108) are given in Table 15.80.

Table 15.75. The symbols of functional groups of secondary amines.

Functional Group	Group Symbol
NH group	NH
C-N (methyl)	C-N (i)
C-N (alkyl)	C-N (ii)
CH₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H(CH_2)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

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200		no parameters of sect	ondary amines and	experimental values	1							
rarameter	Group	C-N (i) Group	C-N (ii)	C-H (CH <sub>3</sub> )	C-H (CH <sub>1</sub> )	dnouD Group	C: - C: (a) Group	ر-د (ہ) وہمتا	C-C (6)	C-C (d) Group	C-C (e) Group	C-C (f)
o (a)	1.26224	1.94862	1.94862	1.64920		1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2 10725
c, (a,)	0.94811	1.39593	1.39593	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1 45164	1 45164
Bond Length 2c' (A)	1.00343	1,47739	1.47739	1.10974	1,11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.00 (dimethylamine)	1.455 (dimethylamine)		1.107 (C H propane) 1.117	1.107 (C - H propane) 1.117	1.122 (isobutane)	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531
h,c (a,)	0.83327	1.35960	1.35960	1,27295	1.29569	1 29924	(butane)	(butane)	(butane)	(butane)	(butane)	(butane)
ъ	0.75113	0.71637	0.71637	0.63580	0.63159	0.63095	009890	0098910	06/26/1	01046.1	1.52750	1.52750
									2000	3	90000	XXXX

Dond							İ								
Polito	Atom	f,	E,	E,	E,	Final Total	, and	, de	Eratum	E(C2sa)	.0	9	9	P	1
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Signal Control	(a°)	(°)	Final	(eV)	Đ	· ©	·©	(°)	(%)
H,C,N(C,H,)-H	2	-0.56690	-0.56690	٥	•		0.93084	0.85252	-14 01054	ŀ	65 61	18			
-H1C,N(Rura)-H	N	-0.56690	-0.36690	۰	۰		0 93084	0800	14 95044			1,02	O. 1	U.34340	0.40264
H,C, -NH -C,H,	ن	-0.56690	٥	°	٥	9521 251-	12210	Cosso	20000	200000	118.18	78'10	8.40	0.54546	0,40264
H,C, - NH - C,H,	2	-0.56690	-0.56690	°	0		0 93034	2000	15 05054	e/ log ct.	84.14	83.88	40.30	1.48625	0.09032
-H,C,-NH-C,R	ن	-0.36690	-0.92918	۰	•	2111181.	11110	0 83360	1016031	1	66.00	0.66	38.26	1.53008	0.13415
-H3C, -NH-C,H3-	2	-0.56690	08995 0	c			1	And the second	1007501	-10.13097	78.89	2.10	36.99	1.55650	0.16057
( = H (CH)							0.33084	U.5252	-15.95954		80.95	99.05	38.26	1.53008	0.13415
(200) 11 - 3	ا	-0.92918	۰	0	0	-152.54487	17716.0	0.86359	-15.75493	-13.56407	SV LL	102.51	41.48	1,23564	0.18708
$C = H (CH_2)$	ن	-0.92918	-0.92918	0	0	-153.47406	17716,0	0.81549	-16.68412	-16.49325	68.47	11.53	35.4	1.35486	0.29913
C-H(CH)	C	-0.92918	-0.92918	81626.0-	٥	-154,40324	0.91771	0.77247	-17,61330	-17.42244	69.10	118.90	1	1 43088	2,440
$H_3C_3C_4H_3CH_3-$ (C-C (a))	ن'	-0.92918	٥	0	o	-152.54487	0.91771	0.16359	-15.75493	-13.56407	53.82	116.18	30.08	6,813	0.38106
H,C,C,H,CH, -	౮	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16 68412	AC107-91-	3	5	10,2	-	
חטרומ - טרו איני ארבים												,	20.00	1.50630	0.43117
(C-C(b))	ť	-0.92918	-0.92918	-0.92918	o	-154,40324	1771	0.77247	-17.61330	-17.42244	48.30	07.161	21.90	1,97162	0.51388
$(R-H_2C_s(R^2-H_2C_s)C_k(R^2-H_2C_s)CH_2-$ $(C-C_s(c))$	5	81676.0-	-0.72457	-0.72457	-0.72457	-154.71160	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$loc_{\mathcal{C}}(H_{i}C_{i}-R^{i})HCH_{i}-(C_{i}-C_{i}(d))$	Ċ,	81626'0-	-0.92918	-0.92918	0	-154,40324	17716.0	0.77247	-17.61330	-17.42244	3	131.70	21.90	1,57162	0.51388
$terC_s(R^n - H_sC_s)C_s(R^{n_n} - H_sC_s)CH_s - (C - C'(e))$	ζ,	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	err.cr.51.	50.02	129.96	27.66	1.94462	0.49298
$ter(C,C,(H,C,-R)HCH_1 - (C,-C,(f))$	ť	-0.72457	-0.92918	-0.92918	÷	-154,19863	17716.0	0.78135	-17,40869	מתובתו-	52.78	127.22	2,04	1.9240	0.47279
$lsoC_{*}(R^{+}H_{*}C_{*})C_{*}(R^{+}H_{*}C_{*})CH_{*} - (C - C (f))$	Ů,	-0.72457	-0.72457	-0.72457	-0,72457	-154,51399	14150	0.76763	-17.92866	erter.r1.	\$0.04	129.96	27.68	1.94462	0.49298

Descriptions On the Carlot	את	(i) N = J	(i) V = 0	7,5	7.5	B-C	C-C (a)	C-C (B)	(9) 2-2	(P) 2-2	(e) 2-2	(f) 2-2
	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
n,	-	1	_	3	2		1	1	1	1	1	1
n,	0	0	0	2	-	0	0	0	0	0	0	0
B.	0	٥	0	0	0	0	0	٥	0	0	0	0
	0.75	. 0.5	0.5	0.75	0.75	0.75	0.5	5.0	5.0	0.5	0.5	0.5
·	0.93613	1	_	-	-	1	1	1		1	1	-
c.	0.75	-	_	-	-	-	-	-	-	ı	1	1
C,	0.93383	0.91140	0.91140	17110	0.91771	0.91771	17716.0	177160	17210	17716.0	17716.0	177160
63	_	0		0	-	ı	0	0	0	11	1	0
	1	2	2	1	-	_	2	7	7	7	2	2
	-	0	0	3	2	-	0	0	0	0	0	0
	0.75	1	_	0.75	0.75	0.75	0.5	0.5	5.0	£.0	0.5	0.5
-	-	1	-	-	-	1	-	-	1	ı	_	-
V, (aV)	-39,21967	-31.98456	-31.98456	-107.32728	-70,41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (aV)	14.35050	9.74677	9.74677	38.92728	25.78002	12.87680	9,33352	9.33352	9,37273	9,33352	9.37273	9.37273
' (eV)	15.53581	8,20698	8.20698	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	00506'9	6.90500
7, (a7.)	-7.76790	-4.10349	4.10349	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(-vo no) (aV)	-14.53414	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
DEniza (so no) (al)	0	-1.13379	-1.13379	o	0	0	0	0	0	0	0	٥
Er ( 10) (cV)	-14,53414	-13.50110	-13.50110	-15.55407	-15,56407	-14.63489	-15.56407	-15.56407	15.35946	-15.56407	-15.35946	-15.35946
G (nim) (cV)	-31,63541	-31.63540	-31.63540	-67,69451	-49.66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31,63535	-31,63535
$E_r \left( atum - atum, msp^3, AO \right) (eV)$	0	-1.13379	-1.13379	0	0	0	-1.85836	-1.85836	-1.44915	-1,85836	-1.44915	-1.44915
Er (un) (eV)	-31,63537	-32,76916	-32.76916	-67,69450	49.66493	-31,63537	-33.49373	-33.49373	-33,08452	-33.49373	-33.08452	-33,08452
w (10" rad/s)	47.06%	15.1983	84.00.92	24.9286	24.2751	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
Ex (eV)	30,98202	10.00377	17.16484	16.40846	15,97831	15,91299	6.21159	6.21159	10.19220	6.2115.9	6.29021	6.29021
E. (uV.)	-0.34836	-0.20505	-0,26859	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Fram (aV)	0.40696	0,12944	0.11159	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.3532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944 [5]	0.12312	0.12312 [2]	0.12312 [2]
12 (aV)	-0.14488	-0.14033	-0.21280	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Emg (aV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E, (imap) (cV)	-31,78025	-32,90949	-32.98196	-67.92207	-49.80996	-31.70737	-33,59732	-33,49373	-33,24376	-33,59732	-33.18712	-33.18712
E (1. 10 KI) (aV)	-14.53414	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
B (6.10 10) (eV)	-13,59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
En County (cV)	3.50582	3,63971	3.71218	12.49186	7,83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

C-C (f) (e) 2~2 Table 15.79. The total bond energies of secondary animes calculated using the functional group composition and the energies of Table 15.78 compared to the experimental values [3].

Formula One of Table 15.78 compared to the experimental values [3].

Group Group Group Group Group G

	Exp. 8		112	(dimethylami	111.8	(dimethylami 107 (dimethylami 107	(propere) 113.8 (propere) 119.8 (butane)	(burns)	(isobutane)			110.8	(septitary)	III.4	(isobutana)	(rsobutune)
	Cal.		11.24	107.27	8 11	108.44	110,49	110.49	109.50	77 00	₹ 60 20	110.67	110,76	177	1173	 !
	, ©	:								1	1		1	1		_
	ø €	>													1	
	ø, ⊙	>	L	_	$\perp$	ļ	69.51	15.69		70.56	70.56					
<u>o</u> )	E,			0	-1.83836				0			-1.85836			-L.85836	
– atom, msp <sup>3</sup> .A	25		1,01756	0.95917	0.79816	1.15796			1.15796			0.81349	1.04887	1,04887	1.04887	
$E_r(atom \cdot$	· &-		6.73	0.75	-	0.75			67.0			-	0.75	27.0	0.73	
sed. Br is	: '5		-	-	-				-			-	-	-	-	
ngle were 1	ט		8.0	6.73	-				-			_	0.73	27.0	6.73	
s preceding a	C <sub>1</sub>		0,93383 Eq. (15,117))	0.87418	0.79816	-			-			0.81549	0.91771	0.91771	0.91771	
neters from ti	Aben 1		17716.0	0.91)40 (Eq.	0.79816	0.86359		•	0.16359			0.81549	0.87495	0.87495	0.87495	
on of $\theta_{\star}$ , the para	Atom 2 Hybridization Designation	(Table 15.3.A)	_	z	62	×			æ			ฆ	-	_	-	
the calculation	Ernstean 3		-14.534 4	-15.36407 (Eq.	-17.04640	. =			=			-16.68412 C,	-14.82575 C,	-14.82575 C.	-14.82575 C,	†
tal values [1]. In	Atom I Hybridization Designation	(Table 15.3.A)	z	۲	52				7			n	3	3	~	
na experimen		Aleen 1	-14.82575	-14.53414	17.04640	-15.75493			-15.75493			-16.6412	-15.58033 C,	-15,55033	.15.53033	
ioni y muines i	LC Tenninal Alona (a,)		4.0661	3.8123	4.6260	3,4252			3.4252			4.7958	4.1633	4.1633	4.7958	
2	2C Dend 2 ( Q <sub>B</sub> )		2.79186	2.79186	2.79186	2.11106			2.09711			2.91547	2.11333	2.09711	2,903,27	
1000	Bond ( ( O <sub>b</sub> )		2,09711	1.89621	2.79186	2.11106			1,097!!			2.91547	2.91547	291547	72106-2	
Assembly and the parameters from the parameters from the proceeding angle were used. Br is $E_f(atom-atom,my^2,AO)$ .	-	יהכא	(C-N(i)&(ii))	ZHNC, (C-N (i) & (ii))	(C-N (I) & (II)	H".)H7	*27'0'727	Н,2,72	ZHC, H	ZC.C.C.	20,0,0	1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1	ZC,C,H 100 C,	4C,C,H In C,	ישונ". לג"נ"כ"	22.27

Table 15.80. The bond angle parameters of secondary amines and experim

## TERTIARY AMINES $(C_n H_{2n+3} N, n = 3,4,5...\infty)$

The tertiary amines,  $C_nH_{2n+3}N$ , have three C-N bonds to methyl or alkyl groups wherein C-N comprises a functional group. The alkyl portion of the tertiary amine may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise 5 methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in tertiary amines are equivalent to those in branched-chain alkanes.

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In tertiary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3)=-14.63489~eV$  (Eq. (15.25)), and the N AO has an energy of E(N)=-14.53414~eV. To meet the equipotential condition of the union of the C-N  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C-N-bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO~to~N)=0.91140$ .

As given in the Continuous-Chain Alkanes ( $C_nH_{2n+2}$ ,  $n=3,4,5...\infty$ ) section, the energy of each  $C2sp^3$  HO must be a linear combination of that of the  $CH_3$  and  $CH_2$  groups that serve as basis elements. Each  $CH_3$  forms one C-C bond, and each  $CH_2$  group forms two. Thus, the energy of each  $C2sp^3$  HO of each  $CH_3$  and  $CH_2$  group alone is given by that in ethane, -0.72457~eV (Eq. (14.151)), and ethylene, -1.13379~eV (Eq. (14.511)), respectively. In order to match the energy of the component HOs and MOs for the entire molecule, the energy  $E_{T_{otlow}}\left(C-C,2sp^3\right)$  given as a linear combination of these basis elements is -0.92918~eV (Eq. (14.513)). In tertiary amines, the N binds to three  $C2sp^3$  HOs and the corresponding  $E_T\left(atom-atom,msp^3.AO\right)$  of each C-N-bond MO in Eq. (15.52) due to the charge donation

from the C and N atoms to the MO is  $-0.92918\,eV$ . It comprises a linear combination of the energy for a primary amine,  $-0.72457\,eV$  and a secondary amine,  $-1.13379\,eV$ .

The symbols of the functional groups of branched-chain tertiary amines are given in Table 15.81. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 5 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of tertiary amines are given in Tables 15.82, 15.83, and 15.84, respectively. The total energy of each tertiary amine given in Table 15.85 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.84 corresponding to functional-group composition of the molecule. The bond angle parameters of tertiary amines determined using Eqs. (15.79-15.108) are given in Table 15.86.

1. . . . .

Table 15.81. The symbols of functional groups of tertiary amines.	I Group Oroup Symbol	×-7	$C = H\left(CH_3\right)$	C-H (CH.)					(c) (c) (d)		r
Table 15.81. The s	Functional Group	Z.	ՀԴ, քւժսր	CH, group	₹	CC band (n-C)	CC band (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	(0-1 01 ) ))	CC (too iso-C)

	() 2-2	Group		2.10725	1.45164		1.53635		1.532	(propane)	1.531	(butane)		1.52750	
	(a) 2-2	Group		2.10725	1,45164		1.53635		1.532	(propenc)	1.531	(butene)		06/75	9888
	(p)	dnous	0070.0	6.12499	1.45744		1.54280		1.532	(brobane)	<u> </u>	(butane)	1 64616	010401	0 60500
	(3)-0	dnon	2 10936	4.10/23	1.45164		1,53635		1.532	(propare)	157	(Diffanc)	05465	200	0 68888
	('-('b)	2	2.12400		1.45744		1,54280		1.532	(propane)	160	Outable	1.54616	1000	0.08000
	(; - (; (a) Group	1	2.12499	1	1.43/44	-	1.54280	100	755.1	(pinchaile)	(Austral)	1	1.54616	VUYOYU	CONSTR
nmental values   [1]	C-H Group		1,67465	108661	DOCO.		/2011.1		1 133	(isobutane)			47667	500290	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
ary outlies all expe	np C-H (CH.) C-H (CH.) C-H	dinasi.	1.67122	1.05553		11213		1.107	(C-H propane)	1.117	(C - H butane)	1 306.0	60767	0.63159	
	C-H (CH,)	00000	1.04720	1.04856		1,10924		1.107	(C - H propane)	1117	(C-H butane)	1 27395	)	0.63580	
	Group	1 04313	Crear.	1.40112		1.48288			1.458	(trimethylamine)		1.37505		0.71372	
1	rmannacı	0 (0.)		c. (a)	Bond	Length	3c. (A)	_		Ē		h.c (a, )		,	

Table 15.83. The MO to HO intercept geometrical bond parameters of tertiary anines. R.R.R. are H or alkyl groups.	retrical bon(	d parameters of t	certiary ammes.	K, K, K are H	or alkyl groups.	$E_T$ is $E_T(alom-alom, msp^2, AO)$	m – alom, mspʻ								
Bond	Atom	6,	E,	E,	£.	Final Total	[7]	7	Ecolon	$E(C2sa^3)$	.6	9	9	d.	P
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Clay Control	(°)	(g)	(eV) Final	Final	©	·©	·©	(°)	(°)
N-(C,H,),	ن.	-0.46439		٥	0	-152.08028	17719.0	0.88983	-15.29034	B7660.51-	75.03	59.63	40.00	1,50383	0.10271
$N-(C_sH_s),$	٧	-0.46459	-0.46459	-0.46459	0		0.93084	0.83885	-16.21933		78,02	101,98	36.64	1.57525	0.17413
$N-(C_sH_2-)_s$	ن	-0.46459	-0.92918	0	0	-153.00946	17716.0	0.83885	-16.21953	-16,02866	78.02	101.98	36.64	1.57323	0.17413
N-(C,H,-),	2	-0.46459	-0.46459	-0,46459	0		0.93084	0.83885	-16.21953		78.02	86'101	36,64	1,57525	0.17413
$C-H$ $(CH_5)$	ü	-0.92918	0	0	0	-152.54487	17416.0	0.86359	-15.75493	-15.56407	47.49	102.Si	41.48	1,23564	0.18708
$C-H(CH_2)$	Ü	-0.92918	-0.92918	0	0	-153.47406	12416.0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1,35486	0,29933
C-H (CH)	ن	81626.0-	-0.92918	\$1626'0-	•	-154,40324	17719.0	0.77247	-17,61330	-17,42244	61.10	118.90	31.37	1.42988	0.37326
H,C,C,H,CH, - (C, -C (8))	C,	-0,92918	۰	0	٥	-152,54487	17116.0	0.86359	-(3.75493	-13.36407	63.82	116.18	30.08	1,83879	0.38106
H,C,C,H,C'H, – H,C,C,H,C'H, –	٠٠٠	4.92918	-0.92918	o	0	-153,47406	17716.0	0.81549	-16.68412	-16,49325	\$6.41	123.59	26.06	1.90850	0.45117
$R - H_2 C_a(H_2 C_a - R)HCH_1 - (C - C'(b))$	ڻ	-0.92918	-0.92918	-0.92918	•	-154.40324	17116.0	0.77247	-17,61330	-[7,42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2 \mathcal{L}_a(R^a - H_2 \mathcal{L}_a) C_a(R^a - H_2 \mathcal{L}_a) C_H_2 - (C - C \cdot C)$	ڻ	-0.92918	-0 72457	-0.72AS7	-0.72457	154.71860	17710.0	0.75889	-17.92866	enter.71-	48.21	131.79	21.74	1,95734	0.50570
$lsnC_{\mathcal{L}_{\mu}}(H_{\mathcal{L}_{\mu}}-R)HCH_{2}-(C-C^{-1}(d))$	::	-0.92918	-0.92918	.0.92918	۰	-154,40324	17716.0	O.77247	-17,61330	-17,024	4830	131.70	21.90	1,97162	0.51388
$tarC_{s}(R'-H_{s}C_{s})C_{s}(R''-H_{s}C_{s})CH_{s} - (C-C'(e))$	C.	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.7676.5	-17,92866	977.57.71-	\$0.04	129.96	22.66	1.94462	0.49298
lem(C,C,(H,C,-R)HCH,-(C,-C,(f))	C,	-0.72457	-0.92918	81626:0-	٩	-154,19863	17716.0	0.78155	-17.40369	tatieti.	82.78	17.72	24.04	1.92443	0.47279
$(mC_{*}(R-H_{*}C_{*})C_{*}(R^{*}-H_{*}C_{*})CH_{2}-$	53	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17710.0	Q.76765	-17.92866	ert £ 7.71-	50.04	129.96	22.66	1.94462	0.49298

I able 13.84. The energy parameters (6V) of functional groups of services attributes.	rs (ev) or mission	מו בו החתם מו נכונים	y cutti Mas.							
Parameters	C-N Group	C.H.	CH,	H-C Grant	C-C (a)	(a) Claded Claded	Growp Growp	C-C (g)	(e) (f) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	C-C (f)
u'		3	2	-	-	-	_	-	-	
n,	0	2	-	۰	0	0	0	0	0	0
'n	0	0	0	0	0	0	0	. 0	0	0
- C	0.5	0.75	0.75	57.0	0.5	0.5	0.5	0.5	0.5	0.5
ď	_	1	1	_	1	1	1	1	1	1
, c	-	1	-	-	-	1	1	1	1	1
5	0.91140	0.91771	17710	17716.0	17716.0	17710	0.91771	0.91771	17716.0	17716.0
5	0	0	_	-	0	0	0	1	1	0
<b>3</b>	7	-	1	-	2	7	2	2	2	. 2
3	0	9	2	1	0	0	0	0	0	0
ئ	0.5	0.75	27.0	0.75	0.5	5.0	6.5	0.5	0.5	0.5
(,,	-	-	1		1	1	1	1	- 1	1
V, (cV)	-31.67393	-107.32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.101.12	-28.79214	-29.10112	-29.10112
V, (uV)	9.71067	38.92728	25.78002	0894871	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T' (aV)	8.06719	32.53914	21.06675	10,48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (aV)	-4.03359	-16.26957	-10.53337	16242.8-	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3,45250
E(n m) (cV)	-14.63489	-15.56407	-15.56407	-14,63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
DE 4,200 (20 110) (EV)	-0.92918	0	0	0	0	0	0	0	0	٥
E, (w m) (cV)	-13.70571	-15.56407	-15,56407	-14,63489	-15,56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
12, (n. 20) (aV)	-31.63537	-67.69451	-49.66493	-31,63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_r \left( atom - atom, myr^2 .AO \right) (eV)$	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1,44915
Er (sm) (eV)	-32,56455	-67.69450	-49,66493	-31,63537	-33,49373	-33.49373	-33,08452	-33,49373	-33.08452	-33.08452
@ (1013 rouls)	18.1298	24.9286	24.2751	24.1759	6'43699	9.43699	15.4846	9.43699	9.55643	9.55643
Er (aV)	11.93333	16,40846	15.97831	15.91299	65112.9	6.21159	10.19220	6.21159	6.29021	6.29021
En (eV)	-0.22255	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Fra (eV)	0.12944	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,12312 [2]	0.17978	0.09944	0.12312	0.12312 [2]	0.12312 [2]
En (eV)	-0.15783	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (aV)	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803
Erlinan (UV)	-32.72238	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E (4, 17 15) (aV)	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489
E (c. 17 12) (cV)	0	-13,59844	-13.59844	-13.59844	0	0	0	0	0	٥
En (comp) (aV)	3.45260	12,49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.85. The total bond energies of tertiary anines calculated using the functional group composition and the energies of Table 15.84 compared to the experimental values [3].

Formula Name C = N  $CH_3$   $CH_4$  C = C (a) C = C (b) C = C (c) C = C (c) C = C (d) C = C (e) C = C (f) C = C (f)

000

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 . 0.79340 -1,18136   110,41	0.75 . 1,15796 0 108,44	66-51	66-01	0 109.30	70.56 109.44	70.56 109.44	-1.85836 110.67	0 110.76	0	-1.85836	
$C_2$ $C_4$ $C_5$ $C_7$ $C_9$	ļ	1.15796	15.00	15.69	-	70.56	70.56	-1.85836	٥	0	1.15836	
$C_2$ $C_3$ $C_4$ $C_5$ $C_7$ $C_9$	ļ	1.15796	15.00	15 69 31	-	70.56	70.36	-1,85836	0	0	1.85836	
(eV)	ļ	1.15796		86.51	-	70.56	70.56	-1.85836	•	0	1.85836	
٧. «.	ļ	1.15796	·		-			-1.85836			1.85836	
જ	1 1 0.79340	-			T.,			ŀ	1	1	.	
	_	0.75		L	1.15796			0.81549	1.04887	1.04887	1.04887	
	_				0.75			- -	0.75	0.75	a.75	
5		-	-		-			-	-	-	-	
	-	-			-			-	0.75	0.75	6.73	T
C <sub>2</sub> Aloua 2	0,79340	-			-			0.81549	0.91771	17716.0	17716.0	
Alem !	0,79340	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
Hybridization Designation (Table 15.3.A)	9	ж			н			'n	-	_	-	
Alma	-17.!4871	×			H			-16.68412 .0.	-14.83575 C,	-14.82575 C,	-14.82575 C.	
Hybridization Designation (Table 15.3.A)	-	7			7			Ħ	s	-	5	
Alens J	-17.14871	-15.73493			-15.75493			-16.68412 C.,	.15.55033 C <sub>o</sub>	-15,55033 C,	-15,55033 C <sub>k</sub>	
Terrated Assess (a, b)	4.6043	3,4252			3.4252			4,7958	4.1633	4,1633	4.7958	
Demil ( a, )	2 80224	3.11106			1.09711			2.91547	211333	2.09711	2,90327	
Ibmu I ( $\sigma_{_0}$ )	2.80224	2.11106			1120711			2,91547	2.91547	2.91547	2.90327	
	ZC.NC	H. THZ	70'7.70'	H'S'J7	ZHC.H	70,00	2,2,2	, , , , , , , , , , , , , , , , , , ,	т. г. С.	C,C,H B, C,	ב'כ'נ' ב'כ'נ'	- K,C,C,
	$(a_r)$ Towns or Designation Alen 1 Designation Alen 1 Alen 2 Alen 1 Alen 2 $(a_s)$ Alen 1 (Table 153.A) (Table 153.A)	Lone 1 (Cq.) Lone 1 (Cq.) Turnine fautes of Potridization Attent 1 (Attention Attention Attentio	Libral I (q, 1) Libral I (q, 2) Tembel Avers (	Linux 1 ( Q <sub>6</sub> )   Linux 1 ( Q <sub>6</sub> )   Tornital Assess   Hybridization   Hybr	Linux 1 (Q <sub>6</sub> )   Linux 1 (Q <sub>6</sub> )   Tornial Assess   Hybridization Asses   Hybridization	Lineal I (a <sub>q</sub> )   Lineal I (a <sub>q</sub> )   Turnind Asses   Turnind	Lineal I (a <sub>q</sub> )   Lineal I (a <sub>q</sub> )   Turnind Assess   Turnind Assess   Hybridization   Athen 1   Athen 2   Athen 2	Linux 1 (Q <sub>q</sub> )   Linux 1 (Q <sub>q</sub> )   Turnial Avess   Turnial Av	Linux 1 (Q <sub>4</sub> )   Linux 1 (Q <sub>4</sub> )   C <sub>4</sub>   C	Linux 1 ( Q <sub>4</sub> )   Linux 1 ( Q	Limit (q, 1)   Tembel Annea   Graph (Graph and Annea)   Annea   Anne	1,000, 17, 1,000, 17, 1,000,

1

ì

## ALDEHYDES $(C_n H_{2n} O, n = 1, 2, 3, 4, 5...\infty)$

The alkyl aldehydes,  $C_nH_{2n}O$ , each have a HC=O moiety that comprises a C=O functional group and a CH functional group. The single bond of carbon to the carbonyl carbon atom, C-C(O)H, is a functional group. In addition to the C=O functional group, 5 formaldehyde comprises a  $CH_2$  functional group. The alkyl portion of the alkyl aldehyde may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in aldehydes are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that  $E_{mag}$  is not subtracted since unpaired electrons are not created with fragmentation of the CH functional group of aldehydes. The  $CH_2$  functional group of formaldehyde is solved in the Dihydrogen Carbide  $(CH_2)$  section except that the energy of each C-H MO is matched to the initial energy of the  $C2sp^3$  HO (Eq. (15.25)). The C=O and C-C(O)H groups are solved by hybridizing the 2s and 2p AOs of each C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the O AO or between two  $C2sp^3$  HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl aldehydes, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the O AO has an energy of  $E(O) = -13.61806 \, eV$ . To meet the equipotential condition of the union 25 of the C=O H<sub>2</sub>-type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C=O-bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO to O) = 0.85395$ . The unpaired electrons created by bond breakage of the double C=O bond requires that two times

the O2p AO magnetic energy  $E_{mog}$  (Eq. (15.60)) be subtracted from the total energy to give  $E_D(G_{roup})$  (eV) for C=O.

 $E_T(atom-atom, msp^3.AO)$  of the C=O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -2.69893~eV which is an energy minimum for 5 the double bond between the pair of  $C2sp^3$  HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, -1.13379~eV (Eq. (14.247)), and a triple bond, -1.56513~eV (Eq. (14.342)). The triple bond contribution includes the  $C2sp^3$  HO electron of the C-H bond in addition to the pair involved directly in the double bond with O. 10  $E_T(atom-atom, msp^3.AO)$  of the C-C(O)H group is equivalent to that of an alkane, -1.85836~eV, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the aldehyde. In order to match energy between the groups bonded to the C=O, electron-density is shared. Due to the interaction in the transition state between the groups based on the sharing,  $C_{1o}=2C_1$  rather than  $C_{1o}=C_1$  in Eq. (15.52) for the C-C(O)H bond.

The symbols of the functional groups of alkyl aldehydes are given in Table 15.87. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl aldehydes are given in Tables 15.88, 15.89, and 15.90, respectively. The total energy of each alkyl aldehyde given in Table 15.91 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.90 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl aldehydes determined using Eqs. (15.79-15.108) are given in Table 15.92.